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## EXPERIMENTS

AND

## OBSERVATIONS

RELATING TO

ACETOUS ACID, FIXABLE AIR, DENSE INFLAMMABLE AIR, OILS, AND FUEL; THE MATTER OF FIRE AND LIGHT, METALLIC REDUCTION, COMBUSTION, FERMENTATION, PUTREFACTION, RESPIRATION,

AND OTHER SUBJECTS OF

## CHEMICAL PHILOSOPHY.

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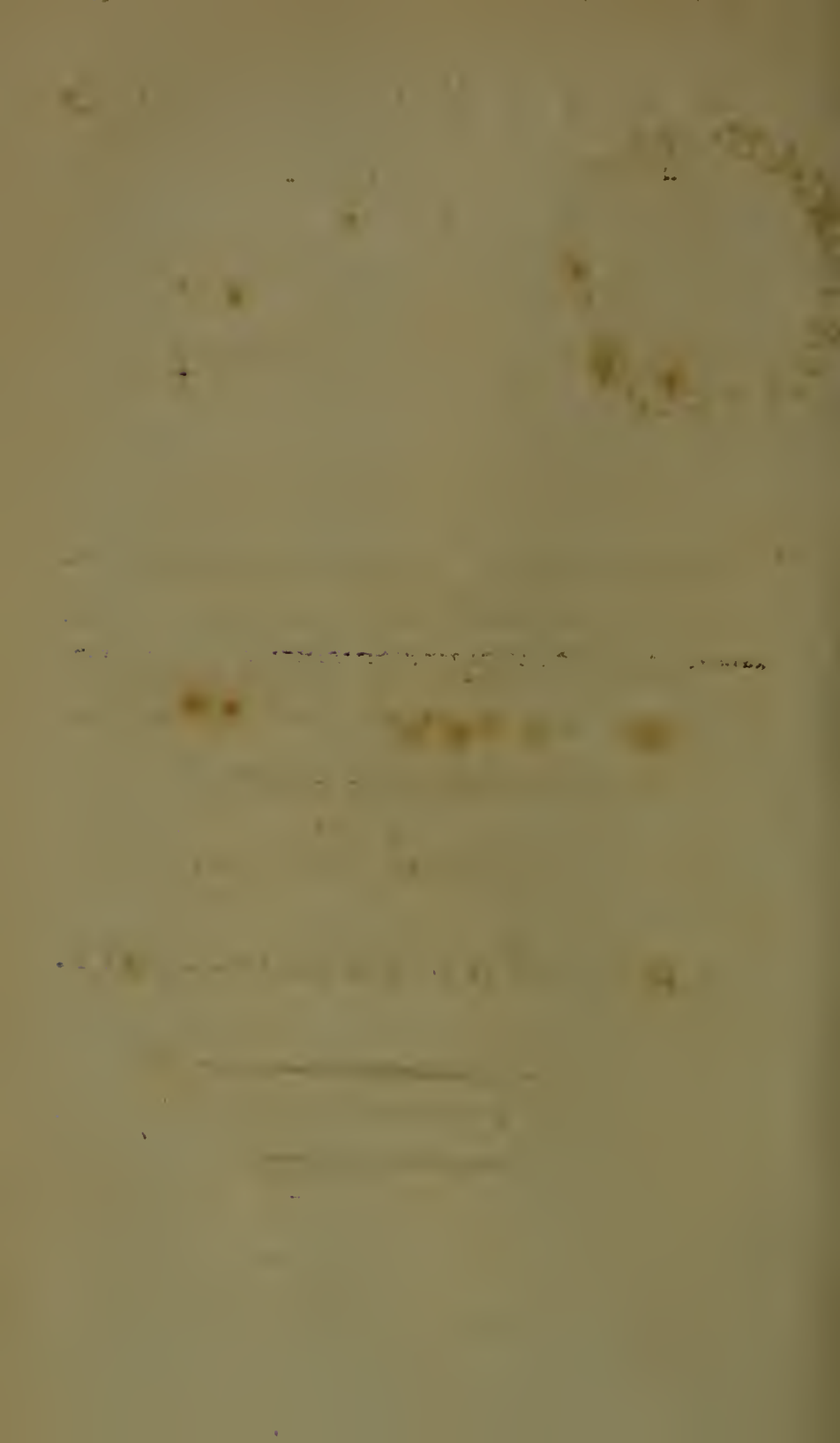
BY BRYAN HIGGINS, M.D.

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L O N D O N:

PRINTED FOR T. CADELL, IN THE STRAND,

M,DCC,LXXXVI.



Under the animating, and FRIENDLY PATRONAGE

Of the MUNIFICENT and MOST NOBLE

HUGH late DUKE of NORTHUMBERLAND

This Volume was commenced and concluded :

To HIM it was to be presented,

The PLEDGE of better Efforts

In his favourite Science :

And NOW

TO HIS EVER HONoured MEMORY,

It is gratefully and piously inscribed,

By BRYAN HIGGINS.



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T H E

P R E F A C E

---

**H**AVING announced this work to many of my friends in the beginning of the last year, when more than a third of it was printed, I think it incumbent on me to relate the circumstances which have delayed the publication of it to this time.

From the beginning of March to the end of July last, all the time that I could spare from the daily

A 4                      duties

duties of my profession, was fully employed with private pupils in preparing for the ensuing Course of Chemistry, and in forwarding their respective pursuits, and afterwards in the incessant business of the experiments and operations exhibited in that Course. During this time it was impossible for me to revise the proof-sheets with the requisite attention, and the printing was necessarily suspended.

In the public proposals for the Course, which commenced in April, the following article appeared:---  
3dly. "*That it shall exhibit the important advances lately made in the knowledge of air and other elastic fluids, of the vegetable acid, phlogiston, fire, and Light.*"

In consequence of this declaration, I introduced in the Course, all that was new in the experiments, or interesting in the doctrines of this volume; and insisted particularly on the circumstances that gave rise to the controversy which was so ably and politely maintained, in the Philosophical Transactions, by Mr. Cavendish and Mr. Kirwan, concerning the principles of fixable air.

By this communication to a very respectable and scientific audience, I deprived the intended work of every advantage of novelty; and having gratified the curiosity of those to whom it was announced, I felt no greater solicitude about the speedy publication of it, than was consistent with my health, and with  
engage-



## x P R E F A C E.

engagements which admitted no procrastination.

During a part of the last summer, I was totally disabled by sickness; and for six months afterwards, all the time that I could spare, was employed in experiments for the perfection of glass for optical use, which I prosecuted with extraordinary assiduity because my venerated patron the late Duke of Northumberland expressed some wishes to this effect, and in enquiries highly interesting to artists who were impatient of delay.

The printing, therefore, was not resumed until last March; since which time, some unexpected delays were made at the press, and lately the publication was deferred on account of  
the

the impending lamentable loss already expressed.

Those who consider that my profession will not permit any seclusion from society, or retirement from interruption, and that in the moments occasionally snatched from these numerous avocations, the most versatile mind cannot apply to a work of this kind, with all the vigour which it might acquire by deliberation or rest; will rather wonder at my attempting to publish a volume, than at the delay, the numerous uncorrected errors of the press and of the author, and that excessive brevity, which requires greater attention in the perusal of many of the following sections, than readers are used to bestow on temporary publications.

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T H E  
C O N T E N T S.

---

S E C T I O N I.

*The preparation of pure acetous acid,  
and acetated vegetable alkali, - 1*

S E C T I O N II.

*Phlogiston is a constituent principle of  
acetous acid, - - - 9*

S E C T I O N III.

*Analysis of acetated vegetable alkali by  
fire, and inductions relative to acetous  
acid, fixable air, inflammable air,  
phlogiston, and fire, - 14*

## S E C T I O N IV.

*Experiments, shewing that in the transmutation of acetous acid into the elastic fluids and oil, there is no intermediate form of it ; and tending to establish the foregoing inductions.* 31

## S E C T I O N V.

*Analysis of acetous calcareous salt by fire, illustrated with general observations,* 44

## S E C T I O N VI.

*Experiments to determine whether the apparent conversion of acetous acid is not owing to the abstraction of some principle of it, as well as to the accession of fire,* - - 77

## S E C T I O N VII.

*Experiments on acetated magnesia supporting the foregoing inductions ; and observations on fuel,* - 89

## S E C T I O N VIII.

*Phenomena of acetous acid in mixture with the vitriolic, and observations generalizing the foregoing inductions,* 98

## S E C T I O N IX.

*Experiments on mixtures of acetous and  
nitrous acid, - - 127*

## S E C T I O N X.

*Experiments and observations relating to  
the principles of acetous acid and fix-  
able air, and the bodies from which  
fixable air is not only extricated, but  
formed; with general interpretations  
of divers interesting phenomena, 143*

## S E C T I O N XI.

*Experiments and observations on acetous  
compounds, containing volatile alkali;  
and reflections on the varieties ana-  
lysis and products of divers substances, 185*

## S E C T I O N XII.

*Preparatory experiments on red led, lith-  
arge and lead, and estimate of the  
matter imbibed or expelled in calci-  
nation and reduction, - 202*

## S E C T I O N XIII.

*Distillation of two pounds of red lead with  
half a pound of acetated vegetable  
alkali, - - - 215*

## S E C T I O N XIV.

*Distillation of eight ounces of litharge with two of acetous acid previously dephlogisticated considerably by vitriolic acid; and formation of fixable air from acetous acid and empyreal air, without ignition,* - 224

## S E C T I O N XV.

*Reduction of litharge and red lead by acetous acid, and the products,* - 236

## S E C T I O N XVI.

*Distillation of litharge with acetous acid, with a view to the mensuration of the water formed, as well as to the other products,* - - - 245

## S E C T I O N XVII.

*Regulization of arsenic by acetous acid,* 255

## S E C T I O N XVIII.

*Products of 16 ounces of litharge and one of charcoal during the reduction,* 264

## S E C T I O N XIX.

*Products in the reduction of litharge and calx of mercury with the smallest quantity of charcoal,* - 274

## SECTION XX.

*Phenomena of the combustion of dense inflammable air, and of substances containing the acetous and phlogistic principles; and mensuration of the products,* 285

## SECTION XXI.

*Primary notions of the matter of fire,* 301

## SECTION XXII.

*Applications of the foregoing notions in the explanation of divers phenomena,* 311

## SECTION XXIII.

*Interpretations of the most important phenomena of combustion, according to the foregoing notions,* - 323

## SECTION XXIV.

*Of Light.* 335

## SECTION XXV.

*Of fermentation, putrefaction, and respiration,* - - 342



# EXPERIMENTS, &c.

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## SECTION I.

*The Preparation of pure Acetous Acid, and Acetated Vegetable Alkali, or foliated Earth of Tartar.*

THE salt called foliated Earth of Tartar is generally made in the manufactories from which the shops are supplied, with pearl-ash and distilled vinegar, and therefore contains some marine salt, and a portion of the oil of vinegar beyond what is necessary to the constitution of acetous acid. These extraneous substances have considerable effect in divers operations, and are apt to perplex or mislead the Experimenter.

The foliated Earth of the Apothecaries' Hall, being prepared for medicinal use only, is indeed tolerably free from marine acid, but by reason of their obedience to the pharmacopœia, which has adopted none of the recent improvements in Chemistry, it is neither so white nor so free from oil as that of the manufacturers.

For these reasons I never employ the foliated Earth of the shops, except for producing a large quantity of Acetous Acid, which by the following treatment I obtain in the purest and most concentrated state.

To a convenient quantity of oil of vitriol in a glass retort, an equal weight of the foliated Earth of Tartar, is to be gradually introduced in small pieces, and at such intervals, that the heat excited shall never exceed 100 degrees of Fahrenheit. If in these intervals the mouth of the retort be loosely stopped, little or none of the acetous vapour escapes; for it condenses in the upper part and neck of the retort, and if this last be duly placed, returns into the charge.

When

When about one-third of the foliated Earth is introduced, the vitriolic acid concretes with it in cooling, and both occupy the bottom of the retort; then the remainder may be introduced at once, without causing any heat or commotion. Thus the salt covers the vitriolic acid, and intercepts any portion of it which might otherwise arise when the charge is heated.

A smaller quantity of vitriolic acid may serve; but as an excess of it is necessary for the total decomposition, and this quantity renders the charge more fusible, I prefer it as promoting equable mixture in a moderate heat, and preventing that decomposition of acetous salt which it undergoes by heat alone, without affording any acid from the portions which escape the action of the vitriolic acid.

The Retort is then to be set in a sand heat, and luted to a long neck, terminating in a tubulated receiver, which delivers its contents through the tube into a bottle, that may be removed at pleasure, in or-

der to keep the successive products apart. No luting ought to be used where the tube enters the bottle ; because the dilated air of the vessels, or the elastic fluids expelled, will force the luting, if the egress elsewhere be prevented, and because there is never any sensible loss of a condensible vapour, whilst the receiver is cool, and the only passage is between the contiguous surfaces which the tube and bottle present to each other.

The distillation is to be carried on very slowly at first, lest the salt last added, by suddenly falling into the liquefied vitriolic mass beneath, should excite so much heat and intumescence as to endanger the vessels, or emit the acetous vapour quicker than the long neck and recipient can condense it.

When as much acetous acid as amounts to half the weight of the acetous salt is distilled, the bottle is to be removed ; and what follows, until a white sulphureous vapour shews itself in the long neck, is to be received in another. This last portion of acetous acid is weak, and slightly impregnated

nated with volatile vitriolic acid, from which it cannot easily be freed. It is therefore to be kept apart.

The former portion is easily purified from the marine acid which rises along with it, in consequence of the decomposition of the marine salt contained in the acetous salt, by distilling it from a twelfth part of fresh *Ter. Foliata*. In this case there is an encrease of the quantity of acetous acid proportionate to the quantity of marine acid absorbed by the alkali of the foliated earth, and expended in decomposing it: and the acetous acid is obtained in a state of purity and high concentration, because this acid is more volatile than water, and the undecomposed part of the acetous salt retains the water until the chief part of the acid is distilled. I generally reserve the first half of this acet. acid for accurate experiments, distinguishing it by the name of *Purified Acetous Acid*, and sometimes, where my notes are literally transcribed, it is called my *Acetous Acid*; the other half serves for any purpose in

which the purity but not the strength or specific gravity of the acid is regarded.

To prepare Terra Foliated Tartari of a purer kind, and which, after the example of the celebrated Bergman, I shall call by the more unexceptionable name of Acetated Vegetable Alkali, I saturate a solution of purified alkali of Tartar, with my purified acetic acid, and evaporate the neutral liquor until it is capable of forming a dry white salt, when cold; in which it never fails, if the evaporation be very slowly conducted towards the end, in a heat not exceeding 212 degrees; and if it be cooled very slowly.

In the preparation of this salt, the following particulars are to be noticed:

In four ounces Troy, or 1920 grains of salt of Tartar, freed from earthy matter, there are 1344 grains of mere alkali, and 576 of fixable air and water.

To



To this alkali an equal weight of water is added, in order to keep the intended neutral salt in solution, without which the point of saturation cannot be ascertained. The strongest and purest acetous acid, whose specific gravity is 1,068, is then poured in, in small portions, at distant intervals, to prevent waste by the intumescence and rapid emission of the fixable air of the alkali, until it is saturated: the saturation is not effected until 1900 grains of the acid are expended.

On evaporating the neutral saline liquor, it continually exhales acetous acid, even when the heat does not amount to 200 degrees. When a dry froth forms on it to the depth of a quarter of an inch, or when a drop taken up on a glass rod sets quickly, and when cold feels dry and pulverable, the evaporation is to be discontinued; for a further continuance or augmentation of heat will decompose the saline matter, and blacken it. At this period, it is the required salt in a state of fusion, which on cooling gradually concretes into a snow



white dry pulverable mass, similar to *Ter. Foliated* in the crystalline lustrated and silvery appearance which it presents when broken into pieces ; and being equally deliquescent, it ought to be guarded from the air.

The dry salt now weighs 2672 grains ; 1344 grains of which being mere alkali, the remaining 1328 grains are acetous acid and water ; and the waste of acetous acid during the evaporation amounts to about 572 grains.

Thus it appears, that even vegetable alkali does not retain as much acetous acid, in the form of a dry salt, as is necessary to neutralize it in water.

## S E C T. II.

*Phlogiston is a constituent Principle of Acetous Acid.*

THE purest concentrated acetous acid is inflammable, but not in a high degree; for by reason of its volatility, and of the water inseparable from it in this form, it eludes in a great measure the ignition necessary for its combustion. But when it is detained by lime, magnesia, metallic substances, or alkaline salts which previous to their combination with this acid were perfectly incombustible, and is sufficiently heated in contact with air, it gives decisive evidence of its combustibility, and shews that Phlogiston is a constituent principle of this acid.

This appears in the most striking manner, in the following experiment :

I saturated fixed vegetable alkali, which had been well calcined, and was perfectly incombustible,

incombustible, with pure acetous acid, and by evaporation prepared the dry acetated vegetable alkaline salt already described. Having then taken the weight of a red-hot shallow earthen dish, after it had been kept two hours in this heat, I placed it in a reddened muffle, and threw on it in successive portions eight ounces Troy = 3840 grains of the salt, to which air was freely admitted, during the whole time.

The salt first melted like wax, with a slight hissing, until some moisture was expelled; soon after it was compleatly fused, it caught fire, and burned with a dense bright durable flame of great volume, and which afforded no visible foot.

After the flame had ceased, that is to say, after the emission of combustible vapour or elastic fluid from the salt had slackened considerably, a black alkaline coal remained, which was still slowly and weakly combustible, and soon became white on the surface exposed to the air. After half an  
hour's

hour's red heat, this salt weighed 2544 grains.

When it was cooled, the whiteness was found to have extended but very little into the mass, which was black every where, except in the surface exposed to the air.

It tasted and dissolved in water like mild fixed vegetable alkali; but the solution was turbid, and blackened by a light coaly powder; which separated by filtration, and washed repeatedly with distilled water, in which it was not at all soluble, weighed when dry, 30 grains. It resembled fine tinder, caught fire freely from a spark, and burned without flame like tinder, until it was reduced to grey ashes, which by slight calcination became incombustible, and were found to be mild fixed vegetable alkali weighing four grains.

The liquor from which this tinder was filtrated, was not found to contain any thing worth notice, except fixed vegetable alkali, combined with fixable air.

Hence

Hence it was inferred, that Phlogiston is a constituent part of acetous acid, and that after a great part of the Phlogistic matter of this acid is expelled from the fixed vegetable alkaline basis of the acetous salt by a red heat, and is expended in the luminous flame and aerial products, a considerable portion of the like matter is obstinately retained in the alkali, wherever the free access of air is interrupted; and that the portion of alkali which remains fully impregnated with this matter, forms with it a black coaly substance, which is insoluble in water, and freely combustible, but without exhibiting any flame; and which consists of about one part of mere vegetable alkali, combined intimately with fourteen or more of pure or compounded Phlogistic matter of acetous acid.

To try whether the acetous acid derives its combustibility, and its capacity to form a combustible substance or tinder with alkalies and indeed with all other bodies with which it is combinable, from some volatile oily matter which is expelled along with

with it, in the decomposition of the acetated salt, and which may not be an essential ingredient of this acid; I have combined the purest part of it with alkali again, and detached it by different mineral acids, and repeated the combinations of it with alkalies, lime, and magnesia, and the decompositions whereby it was separable from them, five or six times; but still found that any salt made with it, and particularly the foliated salt, was still as combustible as that prepared in the manner described in the First Section.

Wherefore I conclude, without awaiting the further proofs which follow, that acetous acid cannot exist, possessing the form and characters by which we distinguish it from others, without a considerable quantity of Phlogiston, and that Phlogiston is a necessary principle in the composition of this acid.

## S E C T. III.

*Analysis of Acetated Vegetable Alkali by Fire, and Inductions relative to Acetous Acid, Fixable Air, Inflammable Air, Phlogiston, and Fire.*

THE apparatus employed in the following experiment consists of a tubulated receiver, whose neck is 12 or 18 inches in length, and duly tapered to receive the neck of the retort, to which I generally cement it with a paste made of liquid glue and fresh powdered lime, which soon acquires a stony hardness, adheres perfectly, is impervious to elastic fluids, and is easily removed after being steeped for some hours in marine acid. By the length of the neck the body of the receiver is kept at a sufficient distance from the hot walls of the furnace; and by its tube it enters the mouth of a separating funnel to which it is accurately ground. The tube is made in the receiver in the part which is lowest, when it is set for distillation, and by this



means all that is condensed runs immediately into the separating funnel, which is provided with a glass cock at the pointed extremity, by the use of which, the successive or different products of the distillation may be drawn off into bottles which fit the extremity of the separating funnel, without suffering any elastic fluid to escape that way, or any external air to communicate with the contents of the vessels.

In the upper hemisphere of the separating funnel, an aperture strengthened with a neck of glass is provided, into which one extremity of a bent glass tube is well fitted by grinding, so as to be perfectly air tight, whilst the other extremity, by the due flexure of the tube, enters a trough of water or mercury, through which it may freely deliver any elastic fluid into the vessels intended for the mensuration of it.

Thus the mixture of elastic fluid and condensable vapour which issues from the charge of the retort, is forced to pass first through the long narrow and cool neck of  
the

the receiver, to circulate in the spacious body of it, to pass again through its narrow tube, to circulate again in the separating funnel; and finally, after depositing all that can be condensed under these advantageous circumstances, the incondensable part passes off through the narrow bore of the bent tube.

Into a strong crown glass retort, well coated with clay, I introduced 16 ounces Troy = 7680 grains of my acet. veg. alkali, consisting of 3862.994 of pure alkali, and 3817.006 of acetous acid and water; and knowing by former experiments that it is impossible to heat this salt to any considerable degree, without boiling it over into the neck of the retort, unless the fire be applied in such a manner as to make the upper part of the vessel hotter than the bottom, I placed the retort on the sand-bed of a reverberatory furnace, with the uncoated extremity of its neck projecting a few inches through the door: and having adjusted the apparatus lately described, to  
the

the uncoated part of the neck, I secured the juncture with glue lute.

The furnace was then gradually heated, and the heat uniformly encreased during six hours.

The quantity of common air in the retort and condensing vessels was 346.5 cubic inches; and the vessels which were ready for measuring the incondensibile product of this charge contained nine cubic inches each.

On the first impression of the fire, the air in the retort being dilated, a portion of it issued, which at the temperature of 52 of Farenheit, and under the mean pressure of the atmosphere, measured 36 cubic inches, and was not different from common atmospheric air. Now water began to shew itself in the recipient, and was afterwards collected to the quantity of 120 grains, when about 63 cubic inches more of common air had issued. The water was not in the least degree acid or coloured, but

C

smelled

smelled and tasted like the oil hereafter described. The last portions of the 63 cubic inches of air, were fit for combustion, but in this respect not quite so good as common air, and smelled like the water. At this period, the emission of air was suddenly followed by a pressure of the external air into the vessels, which would have forced the water, in which the bent tube was immersed, into them, if I had not instantly turned it out of the water, and admitted the air through it.

In distilling any body which contains water, it is to be observed, that the air included in the retort and recipient will be dilated and expelled for the greater part, if not totally, by the watery vapour; and when that vapour no longer issues in due quantity, to fill the vessels and counteract the pressure of the atmosphere, the external air pressing on the vessels, will press into them, wherever it finds admittance; but if the communication is intercepted only by water, or any other fluid, that will be pressed into the recipient, and even into the

the

the retort, so soon as the emission of hot vapour from the charge is insufficient to fill the space which the vapour formerly occupied, after expelling the air.

If external air be admitted to prevent the water from being pressed into the recipient, the quantity of it will be equal to that formerly expelled, provided the distillation be very slowly conducted, as in the present instance. Therefore rejecting from the following measurement the air heretofore expelled, since it was not altered in any considerable degree, we are now to consider the charge as consisting of 7680 grains of the salt exposed to 346.50 cubic inches of atmospheric air; both which amount to 7813.4 grains.

When the fresh emission of air took place, and amounted to 40 cubic inches, I began my reckoning in the following manner :

Cub. Inch. contained.	Of fixed Air.	Of Phlogificated.	Of Inflam.
First 40	6	30	4.0
Next 160	26.7	100	33.3
160	32.	80	48.
160	40	40	80
C 2			The

The water now saved amounted to 340 grains, and ethereal oil began to condense with the last portions of it, for no more water, separable from the oil, appeared after this period.

Cub. Inch. contained.	Of fixed Air.	Of Phlogificated.	Of Inflam.
Next 160	40	20	100
320	80	10	230
320	80	0	240
320	53.5	0	266.5
320	46.	0	274
320	45.7	0	274.3
320	45.7	0	274.3
320	45.7	0	274.3
320	40.	0	280
320	35.5	0	284.5
320	32.	0	288.
320	32	0	288.
320	21.3	0	298.7

Before this period, the distillation of oil had ceased, and now I drew off all that was condensed. It weighed 180 grains.

160	8	0	152
64	2.1	0	61.9

The



The last portion of elastic fluid issued so slowly, although the fire was augmented, and the retort shewed a bright red heat, that very little more was to be expected: I therefore withdrew the fire. The elastic fluid left in the retort and recipients measured, when cold,

Cub. Inch. contained.	Of fixed Air.	Of Phlogificated.	Of Inflamm.
277	15	0	262
<hr/>	<hr/>	<hr/>	<hr/>
Total 5021	727.2	280	4013.8
<hr/>	<hr/>	<hr/>	<hr/>

The inflammable air thus produced, differs greatly in specific gravity from that of metallic solutions; the first portions expelled by moderate heat are much heavier specifically than those which follow at distant intervals, and those that are expelled by the greatest heat at last, are the lightest, but yet greatly exceed the inflammable air from metals, in density and weight.

As it is not necessary to my present purpose, that my mensurations should be perfectly accurate, I shall not insist further on these differences of the specific gravity of



the inflammable air of acetous salt, than to remark, that a mixture of the first and last portions is, according to my experiments, to atmospheric air, in specific gravity, as 19 to 28.84189, and that a cubic inch of this mixture weighs .261 gr. when it is fresh, but freed from fixable air by lime liquor.

Stating a cubic inch of this in-	Gr.
- flammable air at - - -	0.261
A cubic inch of phlogisticated air,	
according to Fontana, at - -	.377
A cubic inch of common air, at -	.385
A cubic inch of pure air, called	
dephlogisticated air, at - -	.42
And a cubic inch of fixable air, at	.57

In the products of the acetous	Grains.
salt, I find, of fixable air -	414.504
Of phlogisticated air - -	105.56
And of inflammable air - -	1047.6018
Total	<u>1567.6658</u>

On the first emission of fixable and inflammable air, a dense white fume fills the long neck and receivers; and these elastic fluids,

fluids, as they issue through the water into the measures, fill these last with fume of the same kind, but not equally opaque. But when the elastic fluids have stood a few minutes, a very small quantity of oily and aqueous matter is deposited, and they become transparent. The quantity of oily matter deposited by 100 cubic inches, was too small to be measured, but some allowance is to be made for it.

During this process, the long neck was cool to the touch within six inches of the luting, at the mouth of the retort, and in all distillations that I have made, in which elastic fluids of any kind are slowly expelled, the heat extends very little farther in the receiving vessels than it would by the approximation of such vessels to the heated retort, if it were quite empty; but condensable vapour carries the heat with it to a considerable distance, and as far as it extends in the state of vapour, from the retort into the extreme condensing vessels. Hence it appears, that elastic fluids retain the fire which issues with them, in a state

of combination, and by virtue of the attraction which causes this union, prevent the escape or diffusion of this fire into the neighbouring bodies or spaces ; and as this phenomenon is common to all the elastic fluids, and almost all experiments in which they are slowly produced, it strongly indicates that a great quantity of fire is combined in every one of them, and is to be considered as a constituent principle and active ingredient.

On breaking the retort, I found a spongy mass, of a black or deep blue colour on the upper surface, and dark grey in the mass, resembling in all respects the black alkaline coal of tartar. It adhered to the glass, and when separated by solution, was found to weigh 5524 grains ; but as the glass had been manifestly corroded in several places, it must have contributed to this weight,

The solution of this alkali shewed a considerable bulk of light black coaly matter,  
which

which was easily separated by filtration from the alkaline liquor which passed limpid, and when washed and dried, weighed 86 grains. It was very like lamp black, caught fire readily like tinder, and burned without smoke or flame to grey ashes, which by calcination grew whitish, or pale yellow, and melted in a weak red heat. The melted matter consisted of vegetable alkali and a little fixable air, and weighed 8 grains; therefore the quantity of volatile combustible matter was about 78 grains.

The filtered alkaline solution from which the coaly matter was separated, was milder and seemed to contain more fixable air than is in ordinary salt of Tartar. In divers experiments it appeared to differ in nothing else from purified salt of Tartar; and even before the coaly matter was separated, it did not act like phlogisticated or Prussian alkali. By neutralizing it with diluted vitriolic acid, I expelled from it 1858 cubic inches of fixable air = 1059.06 grains, which added to 414.504 obtained in the distillation, make 1473.564 grains.

Of

Of 346.5 cubic inches of atmospheric air included in the vessels,  $\frac{4}{3}$  were phlogisticated air, the weight of which is 104.5 grains; and the weight of the pure air in this quantity of atmospheric air is 29.1 gr.: but since this quantity of phlogisticated air is almost equal to that which was expelled along with the inflammable, and we know that phlogisticated air is in no respect altered or active in processes of this kind, we shall reject it as well from our statement of the charge, as from that of the products; and say, that the charge consisting

	Grains.
Of mere vegetable alkali - -	3862.994
Of acetous acid and water -	3817.006
Of pure air - - -	29.1
And altogether amounting to	<hr/> 7709.100 <hr/>
Yielded of mere alkali - -	3862.994
Of fixable air - - -	1473.564
Of inflammable air - -	1047.6018
Of oily matter held in the black coal - - -	78.
Of oil - - -	180.
Of water condensed - -	340.
These amount to - - -	<hr/> 6982.1598 <hr/>

Grains,

Which is less than the charge by 726.9402

This deficiency puzzled me exceedingly, until by repeated experiments similar to this, I found that it is always owing to the water and oil, and chiefly to the water which follows the stream of elastic fluids, and of which a small part remains suspended in them for a considerable time after they acquire the temperature at which I measured their bulk, but not their weight.

Applying these experiments to my present purpose, I may, without any considerable error, state the quantity of water carried off in vapour, and not included in the foregoing weight, at 700 grains; and the quantity of oil carried off in the same way, at 26.9402 grains.

The quantity of water which the 29.1 grains of pure air can furnish in these circumstances, is too small to be regarded on this occasion; and therefore we may say that the acetous salt contained  $340 + 700 = 1040$  grains of water, and consequently

2777.006



2777.006 of mere acid, or mere acid and fixable air: for I strongly suspect that in the mere evaporation and exsiccation of the salt, some fixable air is formed from the acetous acid where it is exposed to the air.

It is to be observed, that the inflammable air, oil, and phlogistic part of the black coal, amount to 1332.542 grains; and the fixable air to 1473.564 grains; the total of which differs from 2777.006, the computed quantity of mere acid, only by the weight of the pure air, which never fails, with ignited acetous salts, to make fixable air. From all which I conclude, that the quantity of matter, in acetous acid thus treated, which is expended in the formation of inflammable air and oil, is not much less than that which is expended in making fixable air; and for the reason above-mentioned, I am of opinion that the weight of these would be equal, if the acetous salt were prepared without exposure to air, which so far as it enters will make fixable air, as will be shewn hereafter.



In this experiment we remark the most illustrative phenomena of a great many more which I have made on salts and vegetable substances, containing the principles of acetous acid; in all which it appears that phlogiston enters the composition of acetous acid in great quantity; that acetous acid detained by its attraction to a fixed body, until it is ignited to a certain degree, forms new compounds; that fire is the only matter which it receives in this circumstance; that it absorbs and combines with this fire, and fixes it; that some principle or principles of the acetous acid combined with fire make fixable air, whilst so much of the remainder as combines in like manner with fire makes inflammable air; and that which escapes the necessary ignition makes oil; or that which is obstinately retained in a fixed body makes a coaly combustible substance.

But above all things we are to observe, concerning the distillations in which acetous acid is submitted to the action of fire, that no part of it either in this or any similar experiment is expelled from acetous salts duly prepared,

prepared, in the form of acetous acid, and that the acidulous liquor, which is said by chemical writers to be distilled in such processes, is not truly acid, but a mixture of water, fixable air, and the ethereal oil of the substance submitted to the distillation.

Finally, it is to be remarked, that in this or in any of the distillations of acetous compounds, made by the ablest chemists, there is no increase of weight in consequence of the new compounds formed by the acetous acid and fire; and consequently all such experiments tend to shew that the matter of fire does not gravitate sensibly.

## S E C T. IV.

*Experiments shewing that in the Transmutation of Acetous Acid into the Elastic Fluids and Oil, there is no intermediate Form of it, and tending to establish the foregoing Inductions.*

**I**N distilling 16 ounces Troy of acetated vegetable alkali in a glass retort set in a sand pot, the absorption of air took place in the manner described in the preceding experiment. Fixable and inflammable air issued also after the salt had been compleatly fused, and the absorption had ceased, but the proportion of fixable air was somewhat less relatively to the inflammable air, from the beginning to the 2340 cubic inch of the mixed elastic fluids; which I impute to the different application of heat.

For here any fixable air, detached from the hottest part of the charge near the bottom of the retort, must pass through the frothy

frothy and colder parts, in which a great part of it may be retained, whilst the inflammable air which is less forcibly attracted by the alkalescent charge, escapes through it undiminished.

When about 3000 cubic inches of elastic fluid were expelled, the quantity of water and oil was nearly the same as appeared at the like period of the former experiment; and now the charge boiled over the helm.

This inconvenience was repeatedly experienced in distilling the same salt in this manner, although I had used retorts capable of holding six times the charge, and had regulated the fire with the greatest caution.

The part of the charge which had not boiled over, was a black spongy alkaline mass, which, when diffused in water, easily deposited a black coaly matter, like that described in the foregoing experiment, on the filter, whilst the alkaline solution passed through quite colourless.

This

This filtered solution evaporated to dryness, yielded pure white and very mild fixed vegetable alkali, which on the affusion of vitriolic acid, yielded a greater proportion of fixable air than is above described, as might be expected in consequence of the heat which it sustained being much weaker and of shorter duration.

The portion which boiled over, and consequently sustained the least heat, was as deliquescent as the acetated alkali employed, and was of a dark brown colour, as if stained by the oil expelled from the part of the salt which occupied the bottom and hottest part of the retort. The solution of it passed slowly through the filter, and was opaque, olive-coloured and greasy, by reason of the oil. The dry salt got from it by slow evaporation, was plainly impregnated with oil, which gave it the colour of pale yellow ochre. Its weight was exactly half that of the white alkaline salt got from the other part of this charge; and with vitriolic acid it yielded fixable air and acetous acid, which left a residue of vitriolic salt, black-

ened by the oily matter. Therefore, the part of the acetous acid which was sufficiently ignited, was all transmuted into elastic fluids and oil, and the remainder retained the form and characters of this acid; and in the transition of acetous acid to form fixable and inflammable air and oil, there is no intermediate form of it; and as the oil may by fire alone be turned into inflammable air, the part which appears in the oily form differs from the inflammable air chiefly in its having escaped the necessary ignition, and consequent disunion of its parts, which must precede its combination with the quantity of fire essential to the elastic form of inflammable air.

In repeating this experiment with 64 ounces of acet. veg. alkali, I observed the same phenomena on a larger scale, and did not obtain one drop of acid. But yet the water impregnated with fixable air and ethereal oil had a pungent acidulous taste; which has misled chemists to consider the like product of acetous salts and vegetable substances as an acid spirit.

In



In these circumstances; the acetous acid does not part in its proper form and constitution from the alkali; but remains in it, until by the access of a certain charge of fire, it forms the new products which pass off in distillation.

In the foregoing manner, 32 ounces Troy of my acetated vegetable alkali were distilled, very slowly, and yielded the water, oil, fixable air, and inflammable air, already described; until, at the expiration of six hours, the charge began to froth and rise towards the helm: then the retort was quickly raised out of the hot sand, without exposing its contents to the atmospheric air. When the matter had subsided a little, and concreted by cooling, it was very spongy at the upper part, but as compact as the foliated Earth of Tartar at the bottom, and equally crystalline, foliated, and deliquescent; but it was of a dark grey colour, and weighed 26 ounces: therefore, only six ounces were expelled in the forms above-mentioned: but in reducing the acetous salt to this state, all the water that could have been withdrawn



without decomposing it totally, was taken from it.

To these 26 ounces I added, very slowly, through a separating funnel, in a tubulated retort fitted to the apparatus described in the Third Section, 26 ounces of the most dephlegmated vitriolic acid, every part of which excited heat, where it acted on the saline mass. By distillation in a sand heat, I obtained first, three ounces of dephlegmated acetous acid ; then as much more of weaker acetous acid ; then two ounces, of which one-third was water ; and lastly, an ounce of acid, equal to dephlegmated acetous acid mixed with its weight of water.

During the distillation of the acid, a dense white vapour flowed down along the lower side of the long neck and receiver, consisting chiefly of acetous and oily vapour and fixable air ; and the elastic fluid which issued through the bent tube of the lower recipient, after the atmospheric air was expelled, consisted of fixable air blended with a little of the oily and acetous vapour. After this,  
half

half an ounce of water, impregnated with vitriolic and sulphureous acid, was distilled, and then the sulphureous or volatile acid, in its elastic state, issued rapidly. At this moment I raised the retort out of the hot sand, and suffered it to cool quickly, without admitting any air to it.

The quantity of water thus procured from the mixture of the most dephlegmated vitriolic acid with highly dephlegmated acetous salt, from either of which separately, no water can be procured by heat, is worthy of notice. The true reason of it will appear hereafter; but when the experiment was made, I imputed it to the agency of Phlogiston, which in divers experiments appeared to facilitate the extrication of water from acids, air, and other bodies; and although I could not determine whether the water was only liberated, or was really formed, I made practical use of the observation; for ever after, in preparing the strongest acetous acid, I was little solicitous about the dryness of the acetous salt, or strength of the vitriolic acid, and trusted

chiefly to the volatility of the acetous acid, by reason of which, the first portions distilled from a great charge are as strong as acetous acid can be procured from the driest materials.

The dense white vapour which occurs in the distillation of this and other acetous compounds, runs distinct under the air left in the vessels, as water runs under oil, and consists of fixable air blended with oily vapour. Whilst the acid arises highly dephlegmated, this fine oil is freely imbibed by it, to a certain quantity; but the diluted acid which follows, becomes turbid with the oil, because it is soluble in water only, in small quantity.

Hence we learn, that the oil or most phlogistic part of acetous acid will unite with the like acid, although the phlogistic part, which has acquired the form of inflammable air, will not. And as this oil may be transmuted into inflammable air by fire only, the agent which gives the elastic form is fire, and that which prevents the  
phlogistic

phlogistic part of acetous acid from uniting with the like acid again, is nothing else but fire.

The saline mass, consisting of vitriolic acid and vegetable alkali, was found strongly impregnated, and quite blackened with coaly matter, like that already described; whence it appears, that vitriolated Tartar, with excess of vitriolic acid, will retain, like alkali, a portion of the Phlogiston of acetous acid in a considerable heat, and will form with it a black coaly substance.

The sulphureous acid shews that the phlogistic matter of acetous acid, volatile sulphureous acid, sulphur, and other bodies, is identical.

From this and the foregoing experiments we may infer, that the fire expended in decomposing acetous acid, passes off along with the products in a fixed state, since they issue cold; and that every portion of the acetous acid requires its due charge of fire, before it can be transmuted by it; since by

withdrawing the charge of acetous salt from the fire, at any time before the whole of its acid is transformed, whatever part of it remains, is still possessed of every property of acetous acid, and affects no condition intermediate between this and the substance of elastic fluids, which with a due charge of fire it never fails to form.

This is manifestly true, with respect to the part of the acetous acid which is expended in the formation of fixable air; but as some of the phlogistic part of the acetous acid is expended in forming oil, whilst the remainder of its phlogistic matter, in new combination, forms inflammable air, the part which is turned into inflammable air, may be said to affect an intermediate form of oil, although the same may not be said of the acetous acid; but still the oil appears to be nothing more than the substance of inflammable air before it combines with fire; for this oil pushed through red hot sand or glass, or clay, or detained in porous bodies by capillary attraction, until it can be duly ignited, is almost wholly convertible

vertible into inflammable air, like that expelled from the acetous salt.

In due time, we shall discover the reason why one part of the acid is expended in making fixable air, whilst the remainder forms a combustible elastic fluid or oil, so different from acetous acid or fixable air.

In these distillations of acetated vegetable alkali, and in those of other acetous salts, in glass vessels, I have always found that more of the fixable air is retained in the alkaline or earthy residue, than is expelled along with the inflammable air.

In fixable air, whose parts are detained and approximated by an alkaline salt, as in our mild alkaline residues of acetous salt; or by earth, as in chalk or magnesia; the matter of fire does not seem to be combined in so great a quantity as in that which assumes the elastic form; but still, we may be allowed to call it, even in the fixed state, by the usual name, and in the latitude of speech which must be admitted in the infancy of  
this



this knowledge, we may say, that fixable air never becomes elastic, until it is saturated with fire, and unrestrained by other matter; for in detaching it from alkalies, chalk, magnesia, or any other body, so as to produce it in the elastic state, we are obliged to use fire; we observe a great expenditure of fire, because the body thus yielding fixable air, never conceives near so much heat, whilst it emits fixable air, as it would in the same fire, if it contained none of this matter; and the fire which thus accompanies fixable air does not desert it, because it does not warm the vessels through which the fixable air runs with a rapid stream: or if we attempt the extrication of fixable air by any other means, we find that nothing void of fire will answer the purpose. Acids cause great heat, and consequently emit a great quantity of fire in combining with pure alkalies, pure calcareous earth, calcined magnesia and divers other bodies; therefore they contain fire abundantly: but when acids are employed to detach fixable air from these bodies, little or no heat is discoverable, no fire is emitted to waste, but all that belonged to



to the acid or alkali, or lime or magnesia, and which cannot be retained in the saline compound, is transferred to the fixable air and combines with it; for otherwise, it would issue hot, and gradually impart this heat to the neighbouring bodies.

Whenever any heat is discovered in the solution of bodies which yield fixable air, and very little else, it implies no more than that the menstruum and solvent together emit more fire in the approximation and union of their parts, than is necessary to the constitution of that quantity of fixable air which issues in the elastic form.

## S E C T. V.

*Analysis of Acetous Calcareous Salt by Fire,  
illustrated with general Observations.*

I HAVE purposely omitted the doubts which may be entertained concerning the foregoing inferences, lest they should perplex the reader, and reserved the discussion of them for the subsequent pages, in which I am to relate the experiments made for this and other purposes.

Suspecting that the alkali of the acetous salt might have contributed to the formation of the elastic fluids, and of the oil especially, by some other means than the mere detention of the acetous acid, until it receives a greater charge of fire than that by which it may be distilled alone without decomposition ; and intending that the measures, by which the real agency of the alkali might be ascertained, should at the same time afford some further elucidation of the nature  
of

of this acid, I made the following experiments with new acetous compounds.

Into a cylindrical glass vessel, filled with mercury, and inverted in a basin of the same, I introduced 240 gr. of powdered lime, and when it had all risen above the quicksilver, I added 720 gr. of concentrated acetous acid, which with a glass rod I mixed briskly with the lime. A heat exceeding 212 degrees was immediately excited, and the mercury was depressed considerably.

The matter which depressed it, occupied a space of 18 cubic inches, under the mean pressure of the atmosphere, whilst it was hot; and was chiefly acetous vapour; for the space lessened quickly as the vessel cooled, and the mercury soon rose to its former height.

By this experiment I discovered the cause of the great waste of acetous acid which I had often experienced, in attempting to make acetous calcareous salt without using

water, in order to save the trouble of evaporation, or to know the degree of concentration or strength at which the acid was contained in the subject to be submitted to the action of fire: even when the acid diluted with an equal weight of water was mixed with quicklime, I observed a considerable waste of the former in pungent vapour, expelled by the heat of the flaking lime, before the intended combination could take place.

When I diluted concentrated acetous acid with equal parts of water, and dissolved a little lime in this weakened acid; and then, in order to have a dry salt directly, poured it on quicklime, I observed that the parts of the lime which were most heated grew black. This is analogous to the change which acet. calc. salt undergoes in the like heat in close vessels; and hence I learned, that in composing this salt, the lime ought to be previously flaked and cooled, and a quantity of water, more than is sufficient for the solution of the calc. salt, ought to be employed, as in the following experiment:

I'

I flaked

I flaked four ounces Troy of pure lime, and when it was quite cold, I added 30 ounces and 8 pennyweights of water, and then 11 ounces 4 pennyweights of concentrated acetous acid: these being the necessary proportions for saturation and solution in the degree of heat excited during the union of the acid and flaked lime, which was about 100 of Farenheit.

I evaporated the solution slowly to dryness, never exceeding 200 degrees of heat; and observed that it exhaled acetous acid sensibly throughout the evaporation, and copiously, when the saline matter grew consistent and approached to dryness, although at this time the heat did not exceed 100. I therefore dried it no further than to render it compleatly pulverable and fit to be easily introduced into a retort, without waste. In this state it weighed 11 oz. 4 dwts. 4 gr. =

Grains 5380

So it consisted of lime        -        -        -        1920

Of acetous acid and water        -        -        3460

And the loss of acid by evaporation

was about        -        -        -        1916

or

or near  $\frac{1}{3}$  of the acid employed : and hence it appears, that near  $\frac{1}{3}$  more of the acid is required for the solution of lime, than is retained in the dry calcareous salt ; or, that dry acetous calcareous salt retains the acid in a more concentrated state than we have it in the purest concentrated acetous acid. But the exhalation of acid throughout the evaporation, and the quantity of acetous acid obtainable from acetous calcareous salt, when decomposed by nitrous and other strong acids, shew that there is a real loss of near  $\frac{1}{3}$  of the acetous acid in evaporating this solution to dryness.

I have often observed, that acetous calcareous salt, which felt perfectly dry and was kept in paper loosely folded, smelled of acetous acid whenever the paper was opened, during two or three months. For this reason, and because the acid varies in quantity as the salt is more or less dried, I noted the quantity of calcareous earth and acid in the calcareous salt, at the time of my using it in any experiment, from which I intended to learn the quantity of fixable  
and

and inflammable air, and of oil and water, which could be produced from it in distillation.

Of the calcareous salt thus prepared, I introduced 3965 gr. containing 1438 of lime, and 2527 of acid and water, into a glass retort well coated, and placing it in a reverberatory furnace, in which the heat might act equally on the upper and lower parts of the charge, I adapted a condensing apparatus, similar to that already described. The retort and recipients contained 231 cubic inches of common air = 88.935 gr. and the measures in which the elastic fluids were to be received, contained 37 cubic inches each.

When fire was applied, the elastic fluids expelled were stated thus :

Cub. Inch.

1. 37 were atmospheric air.
2. 37 were atmof. air more phlogisticated.

A portion of water and colourless ethereal oil was now drawn off, and marked N° 1, and a white vapour appeared in the receiver.



Cub. Inch. contained.      Fixed Air.      Phlogistic. and Infl.

3.                      37                      5                      32

4.                      37                      6                      31

Before this time, a portion of clear oil, inclining to yellow, was saved apart, and marked N° 2.

5.                      37                      12                      25

Another portion of yellow oil was now withdrawn, and marked N° 3.

Inflam. chiefly.

6.                      37                      11                      26

7.                      37                      10                      27

Now the oil N° 4 was drawn off.

8.                      37                      9                      28

Inflammable.

9.                      37                      8                      29

10.                      37                      7.5                      29.5

11.                      37                      7.5                      29.5

12.                      37                      7.5                      29.5

13.                      37                      7.5                      29.5

14.                      37                      7.5                      29.5

15.                      37                      7.5                      29.5

16.                      37                      7.5                      29.5

17.                      37                      7.5                      29.5

18.                      37                      7.5                      29.5

19.                      37                      7.5                      29.5

[ 51 ]

	Cub. Inch. contained.	Fixed Air.	Inflammable.
20.	37	7.5	29.5
21.	37	7.5	29.5
22.	37	7	30
23.	37	6.5	30.5
24.	37	5.5	31.5

No oil appeared to have been distilled since the twentieth measure; I therefore drew off all that was in the recipient, and got none afterwards; this was marked N° 5.

25.	37	5.3	31.7
26.	37	5	32
27.	37	4.9	32.1
28.	37	4.8	32.2
29.	37	4.7	32.3
30.	37	4.6	32.4
31.	37	4	33
32.	37	3.5	33.5
33.	37	3.5	33.5
34.	37	3.4	33.6
35.	37	3.4	33.6
36.	37	3.3	33.7
37.	37	3.2	33.8
38.	37	3.1	33.9
39.	37	3.1	33.9
40.	37	3	34

	Cub. Inch. contained.	Fixed Air.	Inflammable.
41.	37	3	34
42.	37	3	34

Ever after the distillation of oil had ceased, the vapour in the vessels was less opaque.

43.	37	3	34
44.	37	3	34
45.	37	3	34
46.	37	3	34
47.	37	3	34
48.	37	3	34
49.	37	3	34
50.	37	3	34
60.	37 <sup>0</sup>	3 <sup>0</sup>	34 <sup>0</sup>
61.	37	3	34
62.	37	3	34
63.	37	3.1	33.9
64.	37	3.5	33.5
65.	37	4	33
66.	37	5	32
67.	37	6	31
68.	37	7	30
69.	37	8	29
70.	37	8.5	28.5
71.	37	9	28
72.	37	9.5	27.5

	Cub. Inch. contained.	Fixed Air.	Inflammable.
73.	37	9.9	27.1
74.	37	10.2	26.8
75.	37	10.5	26.5
80.	185	52.5	132.5
81.	37	10.5	26.5

At this time the retort was ready to melt, and it was necessary to withdraw the fire. What issued afterwards was retained in a bladder, fastened to the discharging tube of the separating funnel, and these vessels, when cold, contained 232 cubic inches of air, chiefly inflammable, the calcareous earth, or wet bladder, having imbibed the fixable air, if any issued, about the time when the fire was withdrawn.

The sum of the cubic inches of	Gr.
elastic fluids was	- - 3229
Of which the atmospheric air, un-	
altered, made	- - 74
The fixable air	- - 456.2
The inflammable and the phlo-	
gistic air	- - 2698.8

It is to be observed, that in this distillation, no air in addition to that contained

in the recipients was admitted; for as there was no danger of boiling the calcareous salt over the helm, the retort was quickly heated, and if any absorption of the air happened, its place was supplied immediately by the vapours and elastic fluids which issued early and continually from the charge.

By long experience in operations of this kind, I have been convinced that the quantity of fixable air, which the water can imbibe during the measurement, is not considerable, when it is thus mixed with inflammable air, and when the quantity of water employed is not above  $\frac{1}{50}$  of the bulk of the elastic fluids. What is thus imbibed and gradually emitted to waste from the water is, to my apprehension, barely sufficient to compensate for an inaccuracy, in the mensuration, of a contrary tendency, by which we are led to over-rate the quantity of fixable air. For in the agitation of the mixed elastic fluid with lime liquor, the quantity of this last which enters the measure denotes not only the quantity of fixable  
air

air imbibed, but the quantity of phlogistic and inflammable air which is entangled in minute bubbles in the mixture of water and lime; and therefore, if we state the bulk of the fixable air to be equal to that of the liquor which enters the measure, we assume a greater than the real quantity. When the business is steadily conducted, these opposite errors correct each other sufficiently, with regard to the fixable air.

Concerning the inflammable air which is thus lost during the separation of the fixable air, it is to be observed, that it is barely equivalent to the bulk by which we are apt to over-rate the quantity of this elastic fluid, in measuring it soon after it has issued. For in a mixture of fixable and inflammable airs, issuing with a temperature exceeding 52 by a few degrees, the inflammable air is more dilated than the other, or requires a longer time to accommodate itself to the density proper to its mean temperature. Therefore, in measuring it soon after its egress from the charge, I consider the bulk left in the lime liquor as equal or almost equal to that

by which the inflammable air in the measure exceeds the volume to which it would in due time contract in a temperate medium.

By frequent comparisons of the bulks of such elastic fluids, measured at various temperatures, with their bulks at 52, I ascertained the quantity that ought to be deducted from the measures taken at any temperature, exceeding 52; and this was especially necessary in warm weather, or when the laboratory was heated. But in making this deduction from the measured bulk, I found it not expedient, for the reasons already mentioned, that it should be greater with regard to the inflammable than the fixable air.

These observations are applicable especially to the present experiment, in which the elastic fluids were necessarily measured before they had acquired that temperature to which I confine myself in calculating their weight.

Deducting



Deducting then  $\frac{1}{9}$  of the measured bulk of the elastic fluids of this distillation, I stated the mean bulk of the fixable air at 405.512 cubic inches; and that of the inflammable and phlogistic, at 2398.934.

Of 231 cubic inches of air included in the retort and receivers, 74 were expelled without alteration, and 157 only are to be accounted for: but of this quantity 125.6 cubic inches is the bulk of phlogisticated air, which is merely passive, and about 31.4 cubic inches of pure air operate in the process. Deducting, therefore, 125.6 cubic inches from the volume of the inflammable and phlogistic air, which was 2398.934, we shall find the cubic inches of inflammable air alone to be 2272.434.

The pure air measuring 31.4 cubic inches, and weighing 13.188 gr. and being an active matter, is to be considered as a part of the productive charge, which consisting of 3965 gr. of calcareous salt, and 13.188 gr. of pure air, amounts to 3978.188 gr.

On opening the retort when it was cold, I perceived that it had been melted, but the coating had preserved the form of it. The mass contained in it was almost equal in bulk to the calcareous salt employed: it was black and spongy in all parts, except at the bottom, which presented a circular surface, about  $1\frac{1}{2}$  inch in diameter, grey near the centre, but declining to blackness towards the circumference, and the grey-ness extended to the depth of  $\frac{1}{10}$  of an inch at the central part only.

This grey part being contiguous to the sand bed which preserves a red heat for hours after the fire is withdrawn, was longest exposed to the heat; and the change of colour is nothing more than the whole mass would have undergone by a further continuance of the fire, as will appear in subsequent experiments.

The whole weighed 2191 gr. and exceeded the weight of the lime contained in it by 753 gr. Dissolved in dilute marine acid, it afforded 1160.157 cub. inch. of fix-  
able

able air, and 11.5 of dense inflammable air, which, I believe, was held in the spongy mass by capillary attraction: and in the solution it appeared that two or three grains of the glass adhered to the calcareous mass. Thus the whole of the fixable air measured  $405.512 + 1160.157 = 1565.669$  cub. inch. weighing 892.4313 gr. And the inflammable measured 2283.934 cub. inch. weighing 596.1067 gr.

After the fixable air was expelled, I separated the marine solution from the undissolved coaly matter, which, after being well washed and dried, weighed 131 gr. and had great bulk for this weight. It was combustible, but not freely; for it could not catch fire from a flint spark. In the degree of ignition necessary for its combustion, in the slowness of it, and its affording no smoak or flame, it resembled the powder of culm, which is the kind of mineral coal employed, not as fuel but as a phlogistic flux of the Cornish ores of tin. By calcination and frequent agitation in a red heat for three hours, it was reduced to

a grey powder, which clotted in its approach to whiteness, and was found to be calcareous earth, impregnated with a little of the marine acid, which was inseparable, by washing, from the coaly matter. The calcareous earth weighed 41 gr. and therefore, 90 gr. of the coaly powder were dissipated, during the combustion.

When the solution of acetous calcareous salt is inspissated so far only as is necessary for introducing it into a retort, it will necessarily yield in distillation a little acetous acid, or nearly that quantity which would exhale in the exsiccation of it in open air, since it is a property of this salt to hold more acetous acid neutralized in conjunction with water, than it can hold in the dry state. I have accordingly observed in divers distillations of acetous calcareous salt, the quantity of acid was greater from masses barely inspissated, and less when the salt was better dried before the distillation, and least of all, or next to nothing, when it was perfectly dried. But as this treatment was attended with waste of the acid, I preferred the salt  
here

here described for the best experiments; and in my description of the phenomena, I am to observe, that a few drops of the water first distilled were four, but that the quantity of acetous acid which thus escaped undecomposed, was too small to require any further attention.

The portion of watery liquor first distilled, and marked N° 1, weighed 122 gr, was quite transparent and colourless, tasted pungent on the first impression and then left a sense of coldness on the tongue, like peppermint water, and smelled strongly of the ethereal oil which next appeared swimming on the water. It did not catch fire when approached to flame; but when it was suddenly heated by pouring it into a hot spoon, the matter that exhaled from it was inflammable and presented a weak diffusive flame of very short duration: It was nothing more than water slightly impregnated with the subsequent oily liquor.

The straw-coloured oily fluid marked N° 2 weighed 252 gr, smelled like the former,

former, and had a pungent taste, resembling that of acetous ether, but approaching to causticity: advanced within a few inches of the flame of a candle, it caught fire, even when the air was cold, and burned with a durable dense and bright flame, leaving after slow combustion about  $\frac{1}{10}$  of its bulk of water, which tasted and acted in all trials, like water very slightly impregnated with acetous acid.

The yellow transparent liquor marked N° 3 weighed 135 gr, smelled and tasted like N° 2, caught fire from a distant flame, and burned with a clear dense and durable flame, until the whole was consumed, or what remained after slower combustion was only sufficient to bedew the spoon in some parts, or to stain them to a dull yellow colour.

In the distillation of oils expelled from different acetous salts, there is always a very small residue of fixed matter, the quantity of which is greater as the process for obtaining the oil is more rapidly conducted,  
and



and is greatest in those circumstances in which the greatest abrasion of the vessels takes place; for glass vessels suffer this abrasion from watery, oily, or any fluids long agitated in them during evaporation or distillation. In consideration therefore of the fixed matter which may be protruded along with the oil from an acetous salt, by mere mechanical impulse; and of the abrasion which tends to increase the quantity of matter left in the rectification or distillation of such oil; I do not represent the residue in combustion as an essential part of the oil; and since the quantity of it was so inconsiderable, I shall take no further notice of it.

N<sup>o</sup> 4 weighed 178 grains, and differed from N<sup>o</sup> 3 chiefly in its richer yellow or saffron colour, being less transparent, and leaving a dew on the spoon after combustion, which was acidulous and very acrid.

The oil N<sup>o</sup> 5 weighed 168 gr. and differed in no particular worth notice from N<sup>o</sup> 4, except its greater opacity.

On



On pouring portions of these oils to meet in a cylindrical glass tube, and inverting the order of mixture, I could not observe the appearances which indicate a notable difference of specific gravity, although the tenacity or spissitude of the oil last distilled was much greater than that of the first limpid portions, which certainly derive some part of their specific gravity from the water contained in them.

That the oily vapour and oil expelled from acetous salts by fire, possess an inebriating and somniferous quality, I long ago suspected and am now assured by repeated experience: for whenever I smelled the measures recently filled, and breathed the air contaminated with them, for half an hour or more, I felt these effects; but they soon ceased on my retiring into the fresh air.

It now appears, that the ace-	Gr.
tous calcareous salt, weighing	- 3965.
And the pure air	- - - 13.188
Both amounting to	- - <u>3978.188</u>

Gave the following products :

Fixable

Fixable air	-	-	-	-	892.4313
Inflammable air	-	-	-	-	596.1067
Oily matter of the black coal	-	-	-	-	90.
Ethereal and yellow oil	-	-	-	-	733.
Water	-	-	-	-	122.
Lime	-	-	-	-	1438.
All amounting to	-	-	-	-	<u>3871.538</u>

The waste of matter blown away along with the elastic fluids is equal to the difference between the sum of the charge and that of the products, and is 106.65

The quantity of oil wafted in the state of vapour out of the recipients along with the elastic fluids, was very small; but in this and all such experiments, the quantity of watery matter which passes off with them is considerable; and there is no reason to apprehend any important error in our stating the quantity last mentioned of 106.65 gr. as water: wherefore the whole of the water amounted to 228.65 Gr.

And the charge yielded of

fixable air and water	1121.0813
Of inflam. air and oily matter	1419.1067

It will appear hereafter that the pure air, weighing 13.188 gr, contributed to the fixable air and water only, and if we therefore deduct this quantity from 1121.0813, the remainder which is 1107.8933, is the quantity of fixable air and water; and 1419.1067 is that of the inflammable air and oily matter produced from the whole of the acetous acid. Thus it appears that the acetous acid and water, of the calcareous salt, weighing 2527 Gr.

	Grains.
Yielded fixable air and water	1107.8933
Inflamm. air and oily matter	1419.1067
	<hr/>
And yielded in all these	- 2527.
	<hr/>

As the first portions of the oil were found miscible with water, like ether, and water was deposited in the combustion of them, and appeared in some other experiments made with the view of converting it into inflammable air, I am certain that water contributed considerably to the weight of the finer oil, if it be not an essential ingredient of it.

By a review of this experiment, and those of the Third and Fourth Sections, and due consideration

consideration of the established principles of chemistry, we are enabled to make the following observations and inferences.

First; The acid in the dried acetous calcareous salt retains much less water than is contained in dry acetated vegetable alkali; and this is perfectly consistent with the greater affinity of the latter salt to water; for bodies which contain much water, and yet are dry to the touch and pulverable, evidently hold it by chemical affinity. The quantity of water producible from different acetous compounds, may therefore vary considerably, but has no strict connexion with the conversion of the mere acid into fixable and inflammable air.

Secondly; The oily product is much greater from acetous calcareous salt than from acetated vegetable alkali, and the quantity of inflammable air is much smaller. This is to be expected from the weaker affinity of calcareous earth than of alkali to oil, and from the greater quantity of acid in the calcareous salt than in the acetated alkali.

In the first efforts of the fire to decompose or transmute the acetous acid, the fixable air first formed in contact with the lime, adheres to it, and makes mild calcareous earth or whiting, which having a very weak affinity with the phlogistic or oily part of acetous acid, makes little or no resistance to its immediate escape: wherefore this oily part, having nothing capable of detaining it longer in order to subject it to the degree of heat in which it is convertible into inflammable air, passes off by moderate heat in its proper condition, as fast as the part of acetous acid which forms fixable air is separated from it.

In the mean time, as much of this latter part as the calcareous earth cannot retain in the degree of heat which it sustains, passes off in form of elastic fixable air, and mixed with that part of the matter of acetous acid, which having been duly heated before its escape, forms inflammable air.

The smallness of the quantity of inflammable air from the acid of acetous calcareous  
salt,



salt, comparatively with that which is producible from an equal quantity of the same acid detained by fix. veg. alkali, is a necessary consequence of the greater quantity of oil, and shews that the inflammable air is furnished from the principles of the oil, and that the quantity of it is greater or less as the heat is, to which these principles are subjected before they escape from the basis of the acetous salt; all which is conformable to the result of those experiments in which inflammable air is made by heat alone from the oily product of every acetous salt.

Thirdly; The first effect of encreasing heat, towards the conversion of acetous acid into other forms, is to turn a certain part into fixable air, which having no character of a phlogistic body, but all those of an acid, shews that the part of the acid, which is turned into fixable air, consists more of the acid than of the phlogistic matter. But as the remainder of the acetous acid, when deprived of a great quantity of the acid principle, forms oil and inflammable air; as the quantity of oil is greatest when it is

least heated, and least when most heated, or in the greatest expenditure of it in the formation of inflammable air; we may without hesitation repeat the inductions of the former Sections, with this addition; that whilst a part of the acetous acid is by the accession of fire formed into fixable air, the remainder, depositing the greater part of the water proper to concentrated acetous acid or its salts, is disposed to form oil; that the oleaginous matter, when sufficiently charged with fire, deposits its water, and forms inflammable air; but in as much as it is forcibly attracted by a fixed basis, it contributes to the formation of coal.

Fourthly; In the comparison of these experiments we observe, that the quantity of fixable air produced from acetous acid is less as that of the oil is greater; and from this alone we might expect that the oil, however different from acetous acid, contains a great part of the same acid principle which contributes to the formation of fixable air.

That this is at once a true inference and just exposition of the phenomenon, will appear



pear in subsequent experiments; and here I shall only observe that, in distillation, we obtain fixable air from this oil in proportion to the quantity of pure air admitted to it, and the degree of heat to which we expose it: but when the oil, without being exposed much to air, is duly heated, it becomes inflammable air, of which the acid principle is a constituent part. The quantity of fixable air, in this case, is inconsiderable; the quantity of water is greatest from the first or colourless oil, and least from the last portions distilled; and the residue is so small, that we may say, the oil is wholly convertible into inflammable air, the water and fixable air being variable and inessential ingredients, which in my present use of these experiments merit no particular attention.

To transform this or any other essential oil into inflammable air, instead of an iron tube which from its own substance yields inflammable air, I use a glass tube hermetically closed at one end, strongly coated with clay, and fitted at the mouth, by grinding, to a smaller bent tube, which forming

an angle with the large one, may easily transmit the product of the oil, through water, into the measuring vessels. In introducing the oil, I take care that it shall touch no part of the tube, except that which it fills to the height of one or two inches; and then I pour in a mixture of fine white sand and flint powder, in sufficient quantity to imbibe the oil. Placing a column of sand over this charge, to the length of 18 inches or more, I thrust the charged end into the sand-bed of a reverberatory furnace; inclining the tube so, that the sealed end shall be nine inches under the sand, the upper part of the charge about three, and that the greater part of the column of sand in the tube shall emerge and be fully exposed to the action of the fire. In this way, the column of sand is made red-hot before the charge is heated, and when the fire penetrates the sand-bed, or the tube is drawn forward, the oil which expands slowly from the flint powder, is forced to pass through the winding interstices of the reddened column of sand, and issues through the bent tube in the form of inflammable air, carry-

ing oily vapour, of which the quantity is inconsiderable when the operation is well performed.

The oils which yield a greater quantity of fixable air than can be imputed to what they have imbibed, or that which the air admitted can contribute to form, afford nothing contradictory to the foregoing exposition; for I do not assert that oil may not combine with the principles of fixable air, in considerable quantity. On the contrary, I have formerly remarked that concentrated acetous acid unites with the oil of acetous salts, and I have no doubt that it may unite with others. But when any oil yields fixable air abundantly, along with the inflammable, I conclude that, like acetous acid, it contained the gravitating principles of fixable air, and not fixable air already formed; for so innumerable vegetable substances contain them; so mixtures of pure air and this inflammable air contain them, but not fixable air, until they are deflagrated.

Fifthly; Since nothing besides fire is necessary to the conversion of the driest oil  
producible

producible from acetous acid, into inflammable air, and fixable air in small and variable quantity; since nothing else is active in causing those parts of matter, which in the oil were coherent and united, to repel each other and form an elastic fluid; and since from the same oil by the same fire we produce new compounds, viz. fixable air and inflammable air, between the dissimilar parts of which there is also repulsion; we must in conformity to the general and best established principles of chemical union, conclude that fire combines with some principles of the oil, with which it forms molecules, which repel each other by virtue of that fire, and constitute fixable air; that it also combines with the phlogistic part of the oil associated with a portion of the acid principle, and in this combination forms inflammable air, whose molecules repel those of fixable air by the agency of fire only.

Sixthly; From the experiment in which a solution of calcareous acetous salt, poured on fresh lime, is first dried, and then reduced to a black substance, similar to the  
residue

residue left in the distillation of this salt, we perceive that the matter of fire which quicklime holds in combination, and which it emits on the affusion of water, but without exciting illumination, effects the transmutation of acetous acid in the same manner as fire issuing luminous from burning fuel; and therefore, that it is the mere matter of fire, and not a particular motion or modification of it, that produces these changes in the acetous acid.

Seventhly; The accension of the oil produced from acetous acid, by the flame of a candle approached within five or six inches of it, or indeed by a flame two or three feet distant from it in deep vessels, although it be a phenomenon common to many oils and ethers, is not to be disregarded.

Of these the characteristic and rarest oily matter owes its palpable form as much to the pressure of the atmosphere, as to the attraction of the molecules of such oil to each other: for when that pressure is averted, ethers and the finer oils expand, by a great  
part



part or the whole of their matter, into the form of an aerial fluid. During this expansion cold is produced ; that is to say, they imbibe and fix the uncombined fire of the space through which they expand, and of the contiguous bodies. Thus it appears, that these oily bodies attract fire ; that in their aerial or vaporous form, they can fix more of it than in their dense state ; and that the powers which limit their union with fire in their ordinary condition, are the attraction of aggregation, and the concurrent pressure of the atmosphere. All which is exemplified in the rapid emission of fixable air, or nitrous air, or marine acid, or volatile alkali, from water charged with either of these, so soon as we remove a part of the pressure of the incumbent atmospheric air.

## S E C T. VI.

*Experiments to determine whether the apparent conversion of Acetous Acid is not owing to the Abstraction of some Principle of it, as well as to the Accession of Fire.*

**A**LL bodies that contain the acid and phlogistic principles of acetous acid, attract air, and by air duly administered, may be made to furnish salts possessing the acid character, but differing from each other according to the proportions in which these principles are held, and the basis that holds them in combination. Hence the saccharine and other new vegetable acids, which so far as they consist of the foregoing principles, are convertible by fire into fixable and inflammable air, leaving a small residue of the fixed matter peculiar to each of them.

This is our inference from the processes for making the new acids, and from all the experiments for decomposing vegetable  
 substances



substances by fire, from the time of the learned Dr. Hales' to the latest efforts of the assiduous and ingenious Fontana.

But since the works of so many able philosophers tend to impress the notion, that the products of such processes existed already formed in the subjects, and that they are only liberated in consequence of the abstraction of the residuary fixed matter; and since the like reasoning might be thought applicable to my experiments, and consequently to weaken the foregoing inductions; I judged it necessary to make some efforts to prove the total conversion of the mere acetic acid by fire only, in experiments which the inaccuracies of the foregoing could not affect.

I soon found that a great part of what was done with this view, was applicable to greater uses, and I now think that, to avoid repetitions, it ought to be reserved for a future part of this Essay, as the following experiments seem fully sufficient for our present purpose.

The

The earthen retorts generally used in London, are made of the common crucible composition, which consists of powder of baked clay, made plastic with fat apyrous clay and water. These are porous and spongy to a great degree, as may be easily seen by the quantity of water which they imbibe, and for this reason alone the products of acetous salts distilled in them, differ in quantity from those which I have described:

The expedition with which operations must be conducted in my public courses of chemistry, often required that red-hot earthen retorts should be cooled quickly, in order to shew the residuary matter from which elastic fluids were expelled; and on these occasions I observed, that whenever an ounce or more of water was thrown on the reddened vessel, a considerable quantity of elastic fluid, mixed with condensable watery vapour, issued from it. When the water was repeatedly thrown on, until the elastic fluid formerly contained in the retort and its lengthened neck were expelled, what

I followed

followed as the proper aerial product of the water, or of the matter propelled out of the pores of the retort, was always found to be intermediate between atmospheric and phlogisticated air. At first I used this phenomenon to exemplify the porosity and imperfection of these retorts, and I endeavoured to explain it thus. The water is drawn by capillary attraction into the pores at the surface which it first touches, and as it enters these, drives before it to the opposite or internal surface of the vessel, the air which had been lodged in them. This air having been exposed to burning fuel, or meeting the fuliginous matter which the clay might have imbibed, is necessarily more phlogistic than that of the atmosphere; and as the part of the water, which is first and most deeply imbibed, is soonest and most heated, its vapour is determined to expand into the vessel, by the power which propelled the air in the same course: to account for the quantity of air, I had recourse to the observations mentioned in my Essay on Calcareous Cements, page 16.

To this evident permeability of the common retorts, I attributed the waste of water and other products which always occurred in distilling acetous salts in them, but I could not so easily account for another phenomenon which constantly attended this waste, namely, the extraordinary quantity of phlogisticated air, and the increased proportion of the fixable air, relatively to the quantity of the inflammable.

My conjectures on this subject need not be now related, since Dr. Priestley's experiments, communicated to the Royal Society in 1783, relating to the air produced when porous retorts containing water are thus exposed to heat, serve fully to explain these appearances. I was however fully convinced, that the retorts above described were utterly unfit for my chief purpose in these experiments, and I had recourse to those of a more compact kind, with which I was favoured by my most respectable neighbour, the ingenious Mr. Wedgwood.

With these retorts, which I wetted on the outside with a strong solution of borax, I found the acetous salts could be distilled, with very little variation of the products, in fixable and inflammable air especially, from those of the distillations in glass vessels; and the residuary matter did not sensibly differ from what was left in the glass retorts, when the degree and duration of the heat was not greater than they had sustained.

Having distilled acetated vegetable alkali in one of these compact retorts, to the point at which the emission of elastic fluids had formerly ceased, and at which the residuary mass was known to consist of vegetable alkali, fixable air, and alkaline tinter, in the proportions already described; in order to learn what this would yield by mere ignition, I augmented the fire gradually; the effect of which was to expel the fixable air of the alkali, mixed with inflammable air of the same species with the former, but of a lighter kind. The quantity of fixable air was never less than  $\frac{2}{3}$  of all that I had formerly obtained in the saturation of the like

I

alkaline



alkaline coal with marine acid; and the inflammable air bore the like, or rather a greater proportion to the phlogistic matter which was found to reside in the alkaline tinder.

When the emission became very slow, although the furnace was hot enough to melt cast iron, I withdrew the fire; and in the cooled retort I found a solid mass, tasting alkaline and caustic, of a reddish brown colour, and opaque; and the retort was manifestly corroded. The alkali had preyed upon the siliceous matter, and both these on the argillaceous and magnesian of the vessel; and I make no doubt that if it had dissolved more of the substance of the retort, it would have emitted more of its fixable air. This caustic mass, compared with flags made of alkali and Devonshire clay, slightly impregnated with charcoal powder, shewed clearly that its colour was owing to the small remains of the phlogistic matter of the tinder above described; but that no substance decidedly combustible, could be separated from it.

It would be a vain labour to look for any supposititious fixed matter of the acetous acid in this compound of alkali and earths; and so far as this experiment approximated the intended purpose, it shewed, that the part of the acetous acid, which in some experiments remains fixed in the solid combustible substance, only requires more heat to be extricated, and to form inflammable air.

With the same views I made the more satisfactory experiment following.

I expelled the usual products from acetous calcareous salt, heated in a Wedgwood retort as much as the coated glass vessels had formerly been; and when the emission had slackened, or almost ceased for half an hour; at which time, I knew from former experiments, as well as by direct mensuration of the products, how much calcareous earth, fixable air, and coaly matter, was contained in the retort; I encreased the heat as in the last experiment. When no more elastic fluid could be expelled, I removed the retort out of the furnace, to prevent as much



as possible the vitrification of the calcareous earth.

The quantity of fixable air thus obtained by the second or strong heat, was nearly the same as was formerly expelled in the solution of the black residue of acet. calc. salt distilled in a glass retort; and allowing for the rarity of the inflammable air which issued along with the fixable, I found its weight to correspond so nearly with that of the matter expelled in the calcination of the coaly substance which was separated from the black residue of acet. calc. salt, by the solution of the mere calcareous part in marine acid, that I entertained no doubt of the total conversion of that matter which with calcareous earth makes the coal, into inflammable air.

On opening the retort, I found a part of the calcareous residue vitrified, as indeed I expected, where it touched the clay of the retort; but the upper and central parts, to which the vitrification did not extend, consisted of spongy friable calcareous earth,

preserving the figure of the pellets used in the charge, and rather grey and yellow than white. It was soluble without effervescence, excited heat, and flaked on the affusion of water, and possessed every character of pure lime, except its perfect whiteness; but this the best limestone never acquires, when it is reduced to lime in close vessels, for without the aid of air, the phlogistic matter cannot be totally expelled, or to speak in terms less exceptionable to some philosophers, the white colour cannot be attained.

Here I rested in full persuasion that the conversion of the acetous acid does not depend on the abstraction of fixed parts, or the mere expulsion of the volatile from them; but that it is effected by the accession of matter which can be no other than fire, since none other thus pervades glass and porcelain. And now I imagine the reader perceives more distinctly, that the fixable air is formed from acetous acid, so far as the gravitating principles of this air, in combining with fire, lose their former connexion with the other parts of acetous acid; that

that the remainder of this acid, exclusive of water, either is converted into inflammable air, as fast as the fixable air is formed, or is totally convertible into inflammable air, by a due charge of fire ; that the water of acetous acid, or its salts, is passive in these processes, or inessential to the fixable or inflammable airs ; and finally, that the mere acetous acid contains nothing but the gravitating principles of fixable air and dense inflammable air, and requires nothing but fire to form these elastic fluids, whose parts repel each other by reason of the fire only ; because previous to the decomposition, which is effected by an accession, and not by any loss of matter, they attracted and were coherent. Just so, the aerial principle of nitrous acid combines with fire, when a nitrous salt is heated to redness, and forms the elastic fluid called pure air, and easily deposits the concomitant acid, when this also is charged with fire and meets water.

It may not be improper on this occasion to observe, that in distilling acetated calcareous salt in a Wedgwood retort, and suffer-

ing the whole product of condensed water and ethereal oil to remain in the recipient, until the operation was finished, they presented two liquors, perfectly distinguishable, in comparing the upper oily part with the lowest watery fluid, but yet so far blended where they met each other, as to exhibit a gradation from the oily to the aqueous consistence. In pouring the whole into a funnel, in order to separate them, they blended together, and formed a semi-transparent liquor, from which not  $\frac{1}{10}$  of that which before appeared like oil, was afterwards separable. This I attributed to the incapacity of the mild calcareous earth to detain the ethereal oil, until by the abstraction of water, it becomes fatter or more concentrated.

## S E C T. VII.

*Experiments on Acetated Magnesia supporting the foregoing Inductions; and Observations on Fuel.*

CONCENTRATED acetous acid has very little effect on magnesia, until water is added in sufficient quantity to dissolve the salt as fast as it is formed. When mild magnesia is gradually added to the acid moderately diluted, to the point of saturation, the solution has a gluey consistence, and retains a much greater quantity of fixable air than I have ever observed to be held by any other neutral liquor: it also retains this air with greater obstinacy, and sustains a boiling heat for some hours before it parts with the whole of it.

In boiling it froths to the height of a foot or 18 inches, with bubbles, many of them exceeding two inches in diameter, which endure for many minutes, and by  
their

their toughness and opacity, resemble thin bladders.

This saline liquor tastes like the yeast of sweet ales, and in my opinion differs very little from it; for in a cursory analysis, I find yeast to consist of magnesia, combined with the phlogistic, acid and watery matter of acetous acid. By evaporation, this liquor becomes as tough as melted glue, and then dries to a semi-transparent horn-like substance, which adheres strongly to glass or porcelain, and is deliquescent. All this time it exhales acetous acid; and like the calcareous salt, it is found, in its dry state, to retain much less acetous acid than was necessary for the solution of the magnesia.

The continual frothing, and the agitation which is necessary during the evaporation and exsiccation of this acetated magnesia, must promote the absorption of air, if it is disposed to absorb any; and it is with a view to the effects of this air, and the spontaneous escape of a certain part of the acid from this salt, that I notice these particulars.

The



The dry acetated magnesia thus prepared, and distilled in the manner of the calcareous salt, yielded in the same circumstances water, oil, fixable and inflammable air. But the quantity of fixable air, in distillation, was greater relatively to the inflammable; and much less fixable air remained in the residuary magnesia than in the black residue of the calcareous salt. No acetous acid was ever found in the first products of the dry magnesian salt; and the matter left in the retort, after the emission of air had slackened or ceased in a red heat, was black, spongy and friable, so that it could scarcely be handled, without falling into powder.

Vitriolic acid, diluted with an equal or any other quantity of water, shewed no action on this black matter for 30 or 40 seconds; but when the solution became perceptible, it proceeded and increased rapidly with considerable heat. Only a small quantity of fixable air, such as magnesia can retain in a red heat, was emitted during the solution, and a light coaly matter arose  
towards



towards the surface, and remained undissolved in the acid liquor.

This vitriolic solution yielded by evaporation Epsom salt only; and the coaly powder, which resisted fresh vitriolic acid, and was then washed and dried, was found to vary in quantity, with the intensity and duration of the heat to which it had been exposed, and was always combustible and reducible to magnesia, in consequence of the expulsion of its phlogistic matter. This magnesia contained fixable air when the combustion or calcination was slow; but in the contrary circumstances, it was mere magnesia indurated by the heat.

In distillations by moderate heat, the black residue resisted the action of vitriolic acid for the longest time, where it appeared to be best impregnated and defended by the insoluble coaly matter; but the residues which had sustained greater heats, and which dissolved slowly, seemed to resist acids by virtue of their induration or aggregation

3

only.

only. This last is a well known property of magnesia indurated by intense heat.

In divers variations of my experiments on acetated magnesia, I observed the following particulars.

The driest sort yielded more of its acid in the form of fixable air, than any such salt less dried and less exposed to air; and it afforded the smallest quantity of water and oil. When a moist salt was used, the first portions of water were slightly impregnated with acid, and the apparent quantity of oil was greatly augmented, for the true oil blended with a considerable quantity of the preceding or concomitant water.

This, like the oils formerly described, diffused itself in open air, and by its vapour caught fire from a lighted candle placed at some distance. For this, like other volatile oils and ethers, owes its aggregation partly to the pressure of the atmosphere, which it escapes when nothing intercedes them, because it freely pervades the compressing column.

When

When the black coal residue of the magnesian salt was urged with a very strong heat, it emitted a little fixable air, mixed with a much greater bulk of inflammable, and lost proportionably of its weight and blackness, until it became grey, and was reduced to the quantity, or to less than that, of the mere magnesia originally employed. In the fiercest heat it vitrified wherever it touched the earthen retort, and there formed a glassy grey or pearl-coloured slag, resembling that of talc.

When the black magnesian coal was heated to redness in contact with pure air, it entered into combustion, and formed fixable air, of which a part was retained in the magnesia, and the remainder was easily separable from the residuary pure air.

The quantity of fixable air expelled from the magnesian salt, relatively to that of the inflammable, is greatest in the early periods of the process, and gradually decreases to the end; for the magnesia can retain but a small quantity of fixable air in a weak red heat,

heat, but it obstinately retains the matter which by due ignition forms inflammable air.

By the most careful examinations of the different residues of divers processes, I could not discover any matter deposited by the products already described in the magnesia, except the phlogistic, which in distillation formed inflammable air, and by calcination in contact with pure air, yielded fixable air.

From all this it appears, that any quantity of acetous acid that magnesia can detain, until it is sufficiently charged with fire, undergoes the transmutation already described, and is totally converted, not by the deposition of any matter in the magnesia, but by the accession of fire; and the inferences formerly made, are all supported by these experiments, but need not be repeated here.

It is however expedient now to remark, that the very matter which in combination with fire, or by the mere action of fire,  
makes

makes our inflammable air, is strongly attracted not only by fixed alkali and lime, but by magnesia likewise, and with each of these, forms a species of coal or fuel. It is a fact likewise highly meriting our attention, that these most soluble substances, whose appetite of acids is of the strongest kind, become insoluble in their ordinary menstrua, by this union with the matter of our inflammable air, which they thus appear to attract more powerfully than vitriolic acid, and which cannot be expelled from them, except by intense heat, or the concurrent action of fire and atmospheric air.

By thus making artificial fuel, similar to charcoal or coke, and equally insoluble in acids, although containing alkali or soluble earths, we are led to the knowledge of the constituent parts of native fuels. These yield our inflammable air by heat, and contain little more than the gravitating matter of it, which with pure air yields abundance of fixable air, in the combustion of them. Therefore, if an acid principle is necessary to the constitution of fixable air, it is contained

tained in this inflammable air, and consequently, is united along with the phlogiston in all those bodies which are partially or almost totally convertible into this inflammable air by heat, or which in combustion yield fixable air abundantly. Thus charcoal will appear to consist of phlogiston and the acid principle of acetous acid, together with a small quantity of fixed vegetable alkali and calcareous earth; since  $\frac{1}{2}\frac{9}{10}$  or more of common well burned fresh charcoal are convertible into that inflammable air: and our acid principle united with phlogiston, requires very little, if any other matter, in order to form a body highly combustible where fire and air act on it; but otherwise durable, resisting acids, and considerably fixed in close vessels, yet unable even in this circumstance to maintain its aggregation against the utmost force of fire.



## S E C T. VIII.

*Phenomena of Acetous Acid in Mixtures with the Vitriolic, and Observations generalizing the foregoing Inductions.*

WHEN acetated vegetable alkali is decomposed by vitriolic acid, previously diluted with an equal quantity of water, and cooled, there is very little heat or intumescence during the mixture ; and if the acetous salt employed for this purpose is neutral, no fixable or inflammable air appears, and little or nothing issues, until the charge is heated. In distillation, the first portion of acetous acid is strong, but the succeeding are weaker, in regular gradation, until the acid arises, diluted with so much water as scarcely to be equal to distilled vinegar. The residuary mass is vitriolated Tartar, and neither this nor the sides of the retort contiguous to it, shew any blackness or signs of phlogistic matter.

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When the acetated salt is decomposed by the most concentrated vit. acid, and due care is taken, in the manner formerly described, that the heat excited during the mixture shall not exceed 100 degrees; the acid arises highly concentrated at first, but weaker afterwards, and the residuary vitriolated Tartar appears clean and white.

But when highly concentrated vitriolic acid and the driest acetated vegetable alkali in powder, are mixed in large quantity, and equal weight, as quickly as is possible, in earthen ware, a quantity of fixable and inflammable air is immediately discharged along with the acetous product, and is always proportionate to the heat excited in the mixture; the produce in acetous acid is at the same time lessened, and is succeeded by volatile vitriolic acid in considerable quantity. If the fire be withdrawn when this volatile acid arises in thick white fumes, the residuary vitriolated Tartar with excess of vitriolic acid is found blackened with coaly or oleaginous matter, and the sides of the retort shew an oily stain.

In divers experiments of this kind, the acetous acid was exposed to the action of disengaged vitriolic acid, and of the same diluted with water, and never appeared to sustain any change from the mere action of that powerful mineral acid. But when great heat was excited, and this fire co-operated, a part of the acetous acid was transformed into fixable and inflammable air, as it would have been by fire any other way administered, whether the vitriolic acid was used in excess, or only in the quantity necessary for saturating the alkali of the acetous salt; and at the same time a portion of oily matter was detained in the vitriolated Tartar, or phlogisticated the disengaged part of its acid, as any other oil or as charcoal would do. From all which I inferred that phlogiston is attracted more forcibly by the acid principle of acetous acid than by the vitriolic acid in its ordinary form; that this conversion of acetous acid, in the presence of the vitriolic, is effected, not by this last, but by the fire emitted during the union of vitriolic acid with the vegetable alkali; and that in consequence of the separation

paration of the matter expended in the formation of fixable air, the residuary more phlogisticated matter of the acetous acid, forms inflammable air, so far as it meets a due quantity of fire, but otherwise preserves the oily form. A portion of this oil follows and blends with the acetous acid which escapes the decomposition, and the remainder detained in the residuary vitriolic mass, forms a coaly substance, as it does with divers other bodies, or meeting disengaged vitriolic acid, gives the same products as are always observed in the distillation of this acid with oils or charcoal, or any vegetable or other substance which yields fixable air in combustion, and thus appears to contain the acid as well as the phlogistic principle of acetous acid.

To try the validity of these inductions, and the truth of my interpretation of the phenomena, I made the following experiments.

With 16 ounces of the oil of vitriol of the manufacturers, I mixed the same quan-

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tity of concentrated acetous acid, whose specific gravity shewed that it contained an ounce of water beyond the quantity which the strongest acetous acid usually holds.

The heat excited was about 200 degrees, and the mixture in a few hours acquired a pale straw colour. The first 10 ounces of acetous acid distilled from it did not differ in any thing remarkable from concentrated acetous acid, and the residue was transparent, but amber-coloured. Along with the eleventh ounce, volatile sulphureous acid issued, mixed with a very small quantity of inflammable air, and phlogisticated air; but as the quantity of this last decreased very quickly, it was considered as the atmospheric air included in the vessels at the commencement of the operation, the pure air of which was expended on the charge, or in the sulphureous acid which imbibes pure air in the presence of water. Now the liquor in the retort became reddish brown and opaque, and during the distillation of another ounce, which was received apart, the elastic fluids issued more copiously.

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These consisted of volatile vitriolic acid, mixed with about  $\frac{1}{8}$  part in bulk of fixable air, and a quantity scarcely worth notice of inflammable air. The weight of the elastic fluids, acid, water and residuary matter, was very little less than that of the materials of the charge and the pure part of the air of the vessels, and I had no reason to doubt that the small deficiency was owing to the watery vapour which was blown away along with the elastic fluids. Rejecting the last ounce of distilled acid, because it was chiefly water, I saved the preceding 11 ounces for future use,

The residuary acid in the retort was now of a dark red colour, by transmitted light, where it was made to spread thinly on the sides of the vessel; but the whole mass by reflected light looked black, and perfectly opaque.

I mixed the foregoing 11 ounces of acetic acid with 11 of oil of vitriol, by which heat was excited as before, to about 200 degrees. In distilling nine ounces of colour-



less acetous acid from the mixture, I obtained the same products and noticed the same phenomena as appeared in the former process. Reserving this acid, I proceeded until another ounce, consisting of weak acetous acid, impregnated with volatile vitriolic, was collected, and in the mean time, the quantity of elastic sulphureous acid and fixable air, mixed with a little inflammable air, was encreased. The bulk of the fixable air was about  $\frac{1}{8}$  of that of the volatile vitriolic acid as formerly. I then withdrew the retort from the hot sand, and found the acid in it to have all the appearances already described. The weight of this and of the foregoing products was almost equal to that of the acids employed; the deficiency not exceeding what ought to be allowed for the watery vapour blown away along with the elastic fluids.

The nine ounces of acetous acid last mentioned being distilled again with the same quantity of the most concentrated vitriolic acid, presented the same phenomena, with this difference only, that fixable air and  
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volatile sulphureous acid and inflammable air were produced in greater proportion, relatively to the acetous acid: and as the acetous product was next distilled with a double quantity of concentrated vitriolic acid to the same effect, except that the quantity of elastic fluids was augmented, I ceased when the acetous acid was reduced to three ounces, in order to examine it; being already convinced that the whole of acetous acid by this treatment may be reduced to the forms of fixable and inflammable air, and oil capable of affecting the vitriolic acid like other oils and combustible substances.

These three ounces of acetous acid, combined with fixed vegetable alkali, made a fine white foliated salt, as purified acetous acid would do. And this salt in distillation yielded water, oil, fixable air, inflammable air, and a black coaly residue in the proportions formerly described in the distillation of acetated vegetable alkali; and the coaly alkaline residue in like manner yielded fixable air, and the black combustible substance resembling lamp-black,

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The several portions of vitriolic acid, which was thickened and rendered opaque in these distillations, were mixed and distilled, and the condensable product was saved in three separate and equal parts. The first consisted of oil of vitriol, weakened with about two ounces of water, and impregnated with sulphureous acid, and during the distillation of this part, a great quantity of volatile vitriolic acid, mixed with  $\frac{1}{8}$  of its bulk of fixable air, was emitted.

The second portion was oil of vitriol, smelling of sulphureous acid, but clear and colourless, and along with this issued elastic sulphureous acid, mixed with much less fixable air than was in the former; the third portion was like the second, but was not accompanied with so much volatile sulphureous acid: and in the retort I found six ounces of a dark red opaque liquor, of the consistence of treacle, whilst hot, but which concreted in cooling into a wet saline mass, such as might be expected from oil of vitriol, stained by oil, and imbibed by a salt irregularly crystalized. I afterwards found

found that this was nothing more than the vitriolated Tartar, Selenite and Epsom salt, which accompany all the oil of vitriol of the modern manufactories, impregnated with the oleaginous matter of the acetous acid, which every body hitherto tried appears to retain, until it is violently heated or calcined in contact with air.

In all this we see nothing like a dephlogistication or decomposition of the acetous acid by the vitriolic. On the contrary, the acetous acid which arises by moderate heat from the vitriolic, suffers no change; but that quantity of it which can be detained in vitriolic acid, until it sustains greater heat, undergoes the very same transmutation that fire alone always produces, whatever the substance may be that fixes the acetous acid.

We now well know the reason why some part of the decomposed acetous acid became fixable air; why in the moderate heat very little appeared as inflammable air, and much more assumed the oily form; and if the  
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question, implying some fallacy in this reasoning, were proposed, viz. why does the vitriolic acid become phlogisticated? I should answer first, the vitriolic acid becomes volatile or phlogisticated in distillation with any of the substances which yield such inflammable air by heat as the oil of acetous acid affords: all oils and vegetable substances, not excepting the driest, or the charred coal of them, have this effect with vitriolic acid: in other and more general terms, all bodies that contain the same phlogistic and acid principles that reside in acetous acid, render vitriolic acid volatile in distillation: and secondly, without affecting the validity of this answer, founded on known facts, I should say that in all the phlogistications of vitriolic acid that I ever saw, pure air is withdrawn from it: and as in the instance before us, the oleaginous part of the acetous acid forms fixable air, whilst the vitriolic acid becomes volatile, and pure air would also form fixable air with the same oleaginous matter thus heated; I conclude that pure air is more forcibly attracted by this last than by the acid principle



ciple of ignited vitriolic acid, and consequently that this acid, by the subduction of the pure air, and the substitution of phlogiston from the oleaginous matter, makes volatile sulphureous acid. This is sufficient for the present occasion; for it would lead me too far from the objects of this Essay, to enumerate the experiments by which I have been induced to believe that volatile vitriolic acid consists of the vitriolic acid principle combined with phlogiston and fire, whilst the ordinary vitriolic acid is composed of the same acid principle, pure air and water, with less of the matter of fire.

The phenomena of these experiments on mixtures of acetous and vitriolic acid, impressed me with some doubts, which I have not introduced in the relation, because such measures only serve to perplex the reader, in exhibiting the sagacity of the experimenter. To remove these scruples, and look for something further, I varied the experiments in the following manner.

I mixed 24 ounces of strongest acetous acid with 48 of my strongest oil of vitriol.

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The mixture became hot as in the former experiments, and in a few hours had a light straw-colour. In distilling 13 ounces of clear colourless acetous acid from it, the quantity of elastic fluid emitted was not considerable; after the thirteenth ounce, the acid distilled grew gradually and uniformly weaker, and the emission of elastic fluids encreased:

The next seven ounces consisted of acetous acid and about an equal quantity of water considerably impregnated with vitriolic and volatile vitriolic acid; and the next 17 ounces consisted chiefly of vitriolic acid mixed with water and a little volatile vitriolic acid; and during the distillation of these, volatile vitriolic acid in the elastic form issued in considerable quantity, mixed with fixable air and a little inflammable air. The bulk of the fixable air was, as formerly, about  $\frac{1}{8}$  of the inflammable.

As the acid last distilled at this period, was as strong as oil of vitriol, I removed the vessels from the fire. The matter remaining

maining in the retort was opaque, and of the consistence of syrup, when cold, and looked black in the mass; but where it was made to spread thin on the retort, it looked semi-transparent and of a livid red colour.

Rejecting the portions of acid last distilled, because they were diluted with the water which appertained formerly to the part of the acetous acid that was thus decomposed, and with the water which was formed, as will be fully shewn hereafter, by the union of the mere phlogiston of acetous acid with the pure air of the vitriolic, I took the 13 ounces of acetous acid first drawn off, and mixing them with the livid vitriolic residue in the retort, proceeded to distillation. The heat excited during the mixture was not, to my feeling, so great as before, and very little of any elastic fluid issued from the charge, until about nine ounces were distilled; but in drawing off the tenth ounce, volatile vitriolic acid issued copiously and mixed with about  $\frac{1}{8}$  of its bulk of fixable air and a little more inflammable

flammable air than had appeared in former experiments.

The distillation was continued, with the same phenomena, until the matter in the retort was reduced to 24 ounces; and the product, collected after the nine ounces of acetous acid, consisted of vitriolic acid much weakened with water, and slightly impregnated with acetous and volatile vitriolic acid.

Now one purpose of this trial was accomplished; for acetous acid, weighing 13 ounces, and which had been previously exposed to the action of 48 ounces of concentrated vitriolic acid, was as much decomposed in the mixture with the blackened residuary vitriolic acid of the former distillation, as ever the acetous acid had been by an equal quantity of fresh vitriolic acid; and thus the decomposition appeared to have been effected by fire, and not by the vitriolic acid, except so far as it served to detain the acetous acid. The surplus of inflammable air which appeared above the quantities

quantities noticed in former distillations, was owing to nothing more than the incapacity of the blackened oil of vitriol to furnish so much atmospheric air as is contained in the pure and colourless; for the same matter which yields inflammable air, always affords fixable air when under due ignition it meets pure air.

The nine ounces of acetous acid first drawn off in the foregoing distillation, appeared on divers trials to be acetous acid unaltered in every respect, except that it was impregnated with a little of the vitriolic, and contained more water than is proper to our concentrated acetous acid: for in mixture and distillation with fresh concentrated oil of vitriol, it presented the phenomena described in the beginning of this Section; and the portion of it that was distilled unaltered in this process, being divided into two parts; one of them combined with calx of lead and distilled, gave the same products as are obtainable from the like calx combined with my pure acetous acid; and the other part, combined

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with fixed vegetable alkali, made acetated vegetable alkali, which yielded water, oil, fixable and inflammable air, and a black alkaline coal, like those of pure acetated vegetable alkali: and in these trials the vitriolic impregnation was found to be so small as scarcely to deserve any notice.

Wishing to know the condition of the matter that gave the blackness and spissitude to the vitriolic acid remaining in the retort, and which, as I have already shewn, would be expended, if the distillation were continued, in the production of volatile vitriolic acid and fixable air; I diluted the 24 ounces of this acid with 16 of distilled water. In so doing, I observed the same hissing, heat, and pungent vapour as occur in mixing water with concentrated colourless vitriolic acid. But the diluted acid remained opaque, and the opacity was plainly owing to large particles of black flacculent matter, which were diffused through it, and were not disposed to separate by subsidence, or by rising to the surface: in order therefore to effect a separation, by making

the diluted acid pass through a filter without corroding it, I added a quart more of water.

The filtrated liquor shewed a pale yellow colour, and when reduced to eight ounces, or less, by evaporation in the open air, became opaque and livid, as if a part of the oleaginous matter had passed along with the acid and water, through the filtering papers: it also deposited some saline matter, but this was only what originally was contained in the oil of vitriol employed. The matter left on the filter was like lamp-black wetted with weak vitriolic acid, and felt as if it were in a state intermediate between oil and coal. A small portion of it exposed to heat, first exhaled water and vitriolic acid, then became red, and entered into combustion, but without any appearance of flame. By the residue it appeared to contain some salts of the vitriolic acid which might be washed away from it. I therefore washed the mass left on the filter with a quart of water, which being used in suc-



cessive portions, left the black matter free from vitriolic acid, or at least insipid.

The water thus employed being evaporated to an ounce, left about half this quantity of vitriolic acid, which was blackened by the oily matter that followed it through the filter consisting of good paper in four folds, and in cooling deposited some salt of the same kind with that last mentioned.

I had often before observed, that the black residues of acetous salts impregnated the water with which they were washed, so far that in evaporation the last portions of it appeared turbid and black; and I attributed this to the imperfection of the filters; but in these last experiments, and others which they suggested to me, I found that the coaly matter, left in the residue of divers acetous salts decomposed by heat, is in a small degree soluble in water, like selenium or lime, and still more when the water is acidulated.

The black coaly matter that remained on the filter after the ablutions above mentioned, when dried to the consistence of soap, blackened and strongly adhered to every substance on which it was rubbed, and neither alkalies nor any of the mineral acids could efface the traces made with it, but aqua regia seemed to weaken them. It floated in a mixture of equal parts of oil of vitriol and water, but was not dissolved by this, or nitrous, or marine acid; aqua regia seemed to alter the colour of it superficially, but did not act as a solvent. Its weight was three ounces, of which about  $\frac{3}{4}$  were water, which exhaled in drying it to 15 dwts. with a pleasant acid smell, towards the conclusion.

When it was well dried, it resembled Indian ink in the cake, both in the colour and texture as well as in the traces made with it. When it was further heated, the smell was not disagreeable; it contracted to  $\frac{1}{4}$  of its bulk before it caught fire; and this did not happen until it was heated to redness in the open air: then it flamed in

an instant, and glowed with a bright red heat; but in the next instant, the flame, which was thin and small, disappeared. On withdrawing it from the fire, the redness and combustion suddenly ceased, as it happens to culm and other bodies which require great heat and ventilation for their combustion. It took two hours calcination, and free exposure to air by frequent agitation, to deprive it of the coaly character, and to reduce it to a grey incombustible powder, which weighed 48 grains, and by divers trials consisted of magnesian earth.

From the facts related in this and the foregoing Sections, it appears that acetous acid is decomposed in vitriolic acid, in quantity proportionate to the capacity of the vitriolic acid to retain it until it sustains the heat which alone is necessary for the decomposition of acetous acid. That this capacity of vitriolic acid to retain the acetous is as the relative quantity of the former, and depends on a general law. For so vitriolic acid retains water in a degree of heat much greater than water alone can abide,

abide, under the same atmospheric pressure; so all bodies, from which any thing can be expelled by fire, retain the last portions of the volatile matter more obstinately than the first, and compel them to sustain the greater heat. It also appears that when acetous acid is decomposed by fire, in the freest exposure to vitriolic acid, the matter which is capable of forming inflammable air, and which consists, as will fully be shewn in the sequel, of the phlogiston united with some of the acid principle of acetous acid; unites with magnesian earth in preference to the vitriolic acid, and forms with it a coaly mass, which may in the common sense of this word be said to be insoluble. Having in former experiments seen magnesia containing only a little of this matter, and perfectly soluble, save only the parts strongly impregnated with it; and now finding that one part of mere magnesia can retain 20, if not any quantity of it, and that the substance thus formed is of the fixed, rather than of the very volatile kind, we readily conceive how this same matter forms such a variety as occurs in nature of com-

buftible bodies, according to the kind and quantity of other matter with which it is combined in them; and why all fuch bodies, whether fpirits, ethers, oils, gums, refin, vegetable extracts and falts, wood, charcoal, mineral fuel, coke, or fubftances referable to thefe heads, yield fixable air in combuftion, and by due ignition in clofe veffels, denfe inflammable air, which likewife yields fixable air in combuftion: and alfo why fixable air is always produced in the phlogiftication of vitriolic acid by the oleaginous part of acetous acid, or by any vegetable, animal or mineral fubftance, containing the acid and phlogiftic principles of acetous acid, and capable of yielding our denfe inflammable air.

In former experiments, the quantity of water that blended with the oil, or was wafted away with the elastic fluids generated from acetous acid by fire, was variable; and there was room for doubting whether the water proper to concentrated acetous acid or its falts, was all deposited during the conversion of the mere acid, or  
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did not contribute to the fixable and inflammable air: but in these experiments with vitriolic acid, wherein the quantity of water left by the decomposed acetous acid could be measured by the specific gravity of the acids distilled compared with that of these acids in the concentrated state in which they were mixed; I was fully persuaded that the acetous acid deposits its water, previous to the conversion into fixable and inflammable air, or into that compound which with divers bodies forms coal; and that water is not a necessary ingredient in any one of those. But I do not insist on this subject at present, because such mensuration would appear exceptionable, not only by reason of the errors to which it is liable, but because it shews a quantity of water which could not, consistently with my former experiments, exist in the concentrated acetous acid. The cause of this phenomenon will be considered hereafter.

In the last mentioned distillation of acetous from vitriolic acid, I was amused with a phenomenon which brought to my recollection



lection some appearances of the same kind which I had noticed on former occasions. When the quantity of acetous acid amounted to about three ounces, and rose in the receiver so high that the distance between its surface and the nozel of the long slender neck of the retort, did not exceed a quarter of an inch, and when the drops fell at the interval of three or four seconds, each of them, rebounding after the fall, and still preserving the globular form, rolled on the acid liquor; and then, after floating in a quiescent state, for five or six seconds, burst suddenly and spread upon it. Some of these globules in their motion struck the preceding ones, and frequently the motion was communicated without either of them bursting for some seconds after they became quiescent.

Afterwards, when the acid in the receiver rose, and was not distant from the nozel of the retort by more than the diameter of a large drop, the liquor which trickled down, did not discharge itself into the acid, either in the foregoing manner, or in that of a column;

lumn ; but it formed globules of six times the former bulk ; each of which, preserving its proper form, sunk by half its diameter into the acid liquor, without mixing with it ; but when the size of any globule encreased to exceed  $\frac{2}{15}$  of an inch in diameter, it then parted from the nozel and spread on the liquor.

All this looked as if each drop carried its proper atmosphere of repellent matter, which it retained for a considerable time, with a force greatly superior to the weight of a grain, for the drop could not, by reason of its mere aggregation, rebound from liquor of the same kind, and roll on it, and dip and swell in it without mixing.

I immediately attempted to produce the like phenomena in distilling water, under the same circumstances precisely ; but without success ; neither could I find them in treating spirit of wine in the same way.

Upon a review of all the phenomena of this kind that I had ever noticed, I am persuaded that the drops of all inelastic fluids  
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carry their respective atmospheres of some repellent matter which is of the fiery kind; and that in most fluids, the density of these atmospheres is rarely sufficient to resist the approximation or union of the drops with such force as to exhibit the appearances above described: but that bodies, whose principles severally attract fire so forcibly as to form elastic fluids with it, maintain denser atmospheres of this matter around their parts or drops, which then repel with greater force; and that the effect of this repulsion is greatest and most durable, when the drops carry with them any elastic fluid, exceeding the quantity which they can retain when cooled. The electricity producible in distillations and evaporations, and the quick evaporation, if not the convertibility of water into an aerial fluid, by the electric matter, are things not repugnant to this notion; which I mention only for its consonance with the agency of fire that occurs in all our experiments.

The mixed elastic fluids lately described were separated and measured in the following manner.

Receiving

Receiving the successive portions through quicksilver, in cylindrical graduated glass tubes of known capacity, I noted the space occupied by each of them, when the mercury within the tube was level with that in the basin in which the tube stood. I then transferred the tube into strong lime water, and admitted as much of it as could, with the assistance of agitation, be employed in absorbing all the volatile vitriolic acid without becoming turbid. Guided by some trials of known mixtures, and contenting myself with an approximation to accurate measurement, I stated half the bulk of the water so admitted to be equal to the whole of the volatile vitriolic acid, especially when there was a residue of fixable air; for the water thus impregnated with sulphureous selenite and acid, did not in these circumstances appear to imbibe more than half its bulk of fixable air. By washing the remaining elastic fluid in lime liquor, I saw the quantity of residuary air or inflammable air; and deducting the bulk of this and of the volatile vitriolic acid from that of the mixed elastic fluids, I found the measure of the fixable air.

At intervals, I received the mixed elastic fluids in a vessel containing a column of water above the quicksilver ; and as the water in this circumstance imbibed a great quantity of volatile vitriolic acid, and retained little or no fixable air when fully saturated with the acid, the bulk of fixable air emitted in a certain time, was seen ; and in comparing this with the measure of mixed elastic fluids which were expelled in the like time of uniform distillation, I approximated the true proportions of the different elastic fluids ; but not before I had treated the fixable air with lime water in the foregoing manner, in order to separate the volatile vitriolic acid which it carried with it through the column of water, at the period of saturation : Then the fixable air was easily withdrawn from the inflammable, with which it was generally impregnated.

## S E C T. IX.

*Experiments on Mixtures of Acetous and Nitrous Acid.*

TO any man that considers the varieties in smell, taste, medicinal effect and technical use of the substances, whose products, by the sole action of fire, differ in little or nothing except the proportion of them to each other, as appears in the works of Geoffroy, Hales, Newman, Cartheuser, Fontana and others; it is manifest, that our knowledge of the principles of vegetable substances and of bodies which resemble them in composition, has been remarkably defective: and the experiments which throw new light on a subject so extensive in nature, and so interesting to medical practitioners, as well as to divers artists, must appear highly important.

With these impressions I undertook many experiments which the avowed purposes of  
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this Essay did not seem to require; but of which I think a few ought to be related as follows, in order to shew their conformity with the foregoing doctrines, and to generalize the inductions which seem to demand our chief attention.

To four ounces of acetated vegetable alkali I added gradually eight ounces of the strongest nitrous acid; for as strong nitrous acid excites considerable heat in mixing it with water only, and the acetous salt always retains some water, the sudden mixture of the nitrous acid with the acetous salt would from this cause alone, cause a degree of heat sufficient to expel some of the acetous acid.

Notwithstanding this precaution, the heat amounted to about 150 degrees, and some nitrous air and vapour was emitted, but the quantity did not much exceed what might be expelled from the same nitrous acid by heating it. In distillation I obtained eight ounces of acid; of which the four first were chiefly acetous and the rest nitrous acid. The colour of the mixed acids was yellower  
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than that of the nitrous acid used, and resembled that of nitrous acid slightly phlogisticated. The dry mass in the retort weighed about four ounces, was perfectly white, dissolved and crystalized like nitre, and in divers trials was found to be true nitre, with excess of nitrous acid.

As the quantity of nitrous acid was twice greater than what was necessary for the decomposition of the acetated salt; and as the acetous acid, in the instant of its expulsion from the alkali, was fully exposed to an equal quantity of strongest nitrous acid, and these acids were exposed in vapour to each other, it was imagined that some change might be produced in the acetous by virtue of the attraction of its phlogiston to the air of the nitrous acid, and that the nitrous acid, thus deprived of its air in the presence of phlogistic matter, would form nitrous air.

But since the quantity of acetous acid was as great as the acetated salt can be made to yield in any decomposition, and the quan-

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tity of nitrous air or vapour was too small to be imputed to any other agency than that of the fire, by which alone the nitrous acid would yield as much as appeared in this experiment; and as the residuary salt, consisting of half the nitrous acid combined with the vegetable alkali of the acetous salt, shewed nothing phlogistic or oleaginous; it appeared that the acetous acid, which can so easily be decomposed by heat, undergoes no such change in the fullest and most advantageous exposure to the strongest nitrous acid.

To be more fully assured of this I distilled the nitrous acid of the foregoing process, with four ounces of acetated vegetable alkali, and obtained the whole of the acetous acid quite clear and colourless: the matter in the retort was white, and consisted of true nitre super-saturated with nitrous acid only. Thus the nitrous acid was found to have undergone no material alteration or loss; and the acetous acid, being afterwards tried in divers combinations, and lastly by fire, shewed no appearance of dephlogistication

or decomposition by the action of the nitrous acid.

With the views already expressed, I mixed eight ounces of acetated lime with the same quantity of strong nitrous acid, and after drawing off the acetous acid and so much of the nitrous as was used in excess, I distilled these with four ounces of the acetous calca-reous salt. The phenomena were such as may be expected by any person acquainted with the foregoing experiment, and gave no indication of material alteration in the nitrous acid, or of any decomposition of the acetous by the mere action of the former. A small portion, indeed, of nitrous and fixable air appeared; but from the quantity of it, and the period of the distillation, in which it was produced, it was manifestly owing to the heat which the charge sustained at the bottom of the retort, where it had clotted, and was most exposed to the fire, after the chief part of the liquid matter had been expelled.

I then wetted 16 ounces of dried and pure nitre in powder, with four ounces of

strongest acetous acid, and added eight ounces of the strongest oil of vitriol, in a glass retort. The phenomena attending the mixture did not differ in any thing remarkable from those which accompany the mixture of such oil of vitriol with dry nitre, except that the vapour which issued was mixed with perhaps a little more nitrous air.

In distilling four ounces of acid liquor from the charge, about  $\frac{2}{3}$  of the common air of the vessels issued, and carried with them about an equal bulk of nitrous vapour, mixed with a quantity of fixable air, too small to deserve particular notice. The condensed liquor consisted of acetous and nitrous acid, and had a high orange colour. After the fourth ounce, the subsequent acid fell in a slender column, almost as fine as horse-hair, from the nozzel of the retort, through the liquor in the recipient which it touched, to the bottom of it; shewing this product to be chiefly nitrous acid; and this last gradually diluted the colour of the first four ounces of acid until it became yellow.

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When the whole of the distilled acids amounted to five ounces, and acetous acid no longer issued along with the nitrous, from the charge, the nitrous acid next distilled was green, as phlogisticated nitrous acid mixed with water always is ; and an elastic fluid began to issue in notable quantity. This consisted of four parts in bulk of dephlogisticated air, mixed with one of nitrous vapour and nitrous air. But this is the proper produce of that part of the nitre which was considerably heated without meeting vitriolic acid in sufficient quantity to detach its acid in the ordinary state of nitrous acid. For some time afterwards, the proportions of dephlogisticated air and nitrous vapour varied as the heat extended higher in the charge ; and as no phenomenon occurred except what is proper to nitre and vitriolic acid strongly heated in these proportions, I put an end to the operation.

The mixed acids thus obtained were kept six months in a close vessel, and distilled by a gentle heat. The portion first condensed to the amount of two ounces was orange-



coloured, and consisted of acetous acid, impregnated with nitrous acid and nitrous phlogistic vapour, which made it look rather opaque, and inclining to olive-colour; but by the succeeding portions of acid, it was diluted to its former yellow colour, and the whole passed over, the last portions being entirely nitrous, without leaving a stain behind. About half a pint of elastic fluid in the mean time issued from the recipient through quicksilver, and consisted of phlogisticated air and nitrous air, mixed with that of the vessels, the bulk of which last is not included in the half-pint. This quantity is too small to denote any notable change of the acids in the distillation, for the mixed acids could retain so much nitrous elastic fluid from the former process, and the phlogistication of the air of the vessels, is the well known result of the absorption of its dephlogisticated part by the nitrous air or vapour.

In this experiment the acetous acid was first exposed to the action of the vitriolic in its most concentrated state; and when  
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this was expended in decomposing the nitre, it was exposed to the strongest nitrous acid in substance and in vapour; and as the distillation advanced, a part of the acetous acid was exposed at once to nitrous acid in hot vapour, and to the pure air of that part of the nitre, which by reason of the deficiency of vitriolic acid, and its vicinity to the hottest part of the sand, was decomposed by heat alone: and as no more of the acetous acid was decomposed or expended in making the nitrous acid red and elastic, than appears always to be when it is retained in such heat; we may truly infer that the acetous acid cannot be decomposed by the mere action of the nitrous, and that in the presence of the water which is a constituent part of these acids in their ordinary condition, the nitrous acid cannot draw the phlogiston from the acetous, so as to exhibit it in a dephlogisticated state.

As water weakens the action of divers bodies on each other, and especially that of acids on inflammable liquors, I had reason thus to impute the inactivity of the nitrous

acid in these distillations, to the water inseparable from both acids in their ordinary form; but in order to try the validity of this notion, I made divers experiments with the strongest nitrous acid and the most dephlegmated oil distilled from acetated vegetable alkali: for seeing that acetous acid may be resolved by fire into fixable air, water and oil; that the two former are not affected by nitrous acid so as to afford new compounds, and that the latter is; I considered this as the only part of the acetous acid on which the nitrous is apt to act, and the most likely to indicate the effects which nitrous acid would produce with the acetous, if it could be procured quite free from water.

The result of the mixture of these was, that when the oil was slowly added to the nitrous acid, and gradually blended with it by agitation in iced water, so that no sensible heat was excited, they mingled freely and perfectly, without emitting or exhaling any thing considerable, except what they severally exhale into the air included with them,

them, previous to any mixture of this kind. The first drops of oil gave the nitrous acid a yellow colour, the next orange; with more it acquired a claret colour, which grew deeper and darker as the quantity of oil increased. The acid nevertheless seemed to have truly dissolved its bulk of the oil, for in a column of a quarter of an inch in diameter, the mixture appeared uniform and transparent. When it was removed from the iced water, and acquired the temperature of the air, which was  $36^{\circ}$  at this time, it began to discharge bubbles, which arose very small from the bottom, and grew larger in their progress upwards through the liquor, as it happens in making nitrous ether; and in the course of twelve hours, a quantity of elastic fluid was emitted, measuring upwards of thirty times the bulk of the mixture. Three - fourths in volume of this elastic fluid were fixable air, and the remainder was inflammable air mixed with nitrous air, the former of which seemed to be nothing more than the proper exhalation of that part of the oil which had escaped the action of the nitrous acid, or which  
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having deposited its water in the acid, assumed this form, as the ethereal part of alkohol is disposed to do in these circumstances.

On the application of heat, the mixture emitted a great deal more of the like elastic fluids ; and when phlogisticated nitrous vapour arose in considerable quantity, I withdrew the fire, knowing from other experiments what the subsequent product would be, and satisfied already in this proof, that the nitrous acid needs no heat beyond 36 degrees in order to act forcibly on this oil.

When the acid and oil were quickly mixed in any order, or in any quantity exceeding a dram of either, the heat and intumescence were very great, and the quantity of elastic fluid suddenly emitted was proportionate to these directly. After it had deposited the condensible phlogisticated nitrous vapour which issued along with it from the boiling mixture, it was found to consist chiefly of fixable and inflammable air mixed with nitrous and phlogisticated air ;

but the proportions of these varied in different experiments with the circumstances of them. By attending to these, I perceived that the inflammable air was produced from the volatile oil which had received the heat of the mixture, but escaped the action of the acid, and that the quantity of fixable air was directly proportionate to the phlogistication of the nitrous acid. Therefore this acid and our oily matter mutually decompose each other, and form new compounds, by virtue of the elective attractions of their principles, and without the aid of extraneous fire; and as a great quantity of fire is emitted during the action of the oil and acid on each other, the quantity of it that exists concentrated and combined in these, is much greater than can be retained in their new products.

In metallic solutions, and in all others, in which the nitrous acid is phlogisticated; in all combustions of phlogistic bodies, in which nitrous acid or nitrous salts, by virtue of the air contained in them, perform the office of the pure part of atmospheric

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phoric air in calcining, deflagrating or detonating these substances; and in every known instance of the phlogistication of nitrous acid, and of the formation of nitrous air from it; the acid principle loses a part or the whole of its pure air, and by receiving phlogiston instead of it, becomes nitrous air. The quantity of disengaged nitrous air that appears in any of these cases depends on the capacity of the materials employed, to retain the pure air of the nitrous acid in preference to the nitrous air, and in these the consequent predominance of pure air may easily be found: hence the nitrated calces of metals yield abundance of pure air and little or no acid, as Mr. Cavendish has well shewn in the instance of *Mercurius corrosivus ruber*. Of all the experiments which clearly evince this deposition of pure air by the nitrous acid, when it becomes phlogisticated, and forms nitrous air, we need only to mention the following.

Nitrous air, whether procured in detonation, in the solution of metals, vegetables, or other phlogistic substances, or in the  
action

action of the nitrous acid and oils on each other, on the admixture of pure air becomes nitrous acid somewhat phlogisticated; and a great part of the pure air thus administered, is actually expended in the formation of the acid, whilst the remainder contributes to the formation of water. In this as well as every other instance of the entry of pure air into a phlogistic body, heat is generated or fire is emitted, shewing that the nitrous air and pure air severally, are capable of holding more fire, than the nitrous acid and water, which they form, can retain.

Aided by these general observations, we may interpret the phenomena of the mixtures of nitrous acid and oil in the following manner.

Whilst the phlogiston of the oil unites with the acid principle of the nitrous acid, the pure air of the latter is transferred to the vegetable acid principle of the oil, and contributes towards the acid characters, which then become as apparent in the fixable air, as the privation of them is manifest  
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in the nitrous air. That this exposition is true will appear from these considerations; that the nitrous air thus formed, requires only pure air to become nitrous acid, and that disengaged pure air, however procured, together with this oil, in the act of combustion in close vessels, yield fixable air and water, and nothing else, except that quantity of the fire formerly combined in the oil and pure air, which the fixable air and water cannot retain: for I purposely reject from our present consideration a small and variable quantity of the elastic fluid called phlogisticated air, which always appears in the above-mentioned processes, and shall be noticed in due time.

## S E C T. X.

*Experiments and Observations relating to the Principles of Acetous Acid and Fixable Air, and the Bodies from which Fixable Air is not only extricated but formed; with general Interpretations of divers interesting Phenomena.*

**I**N addition to the cursory observations formerly made, I am now briefly to relate the general result of the experiments which exhibit the agency of air on acetous compounds.

Having tried every one of the tinder like and coaly substances heretofore described as consisting of oily matter of acetous acid fixed by earth or alkali or neutral salts, by calcining or burning them in contact with pure air; I found the quantity of fixable air produced in these processes to bear a direct proportion to that of the pure air expended in them respectively. In burning the oils of acetous acid with pure air from nitre, the  
product

product was fixable air and water, exclusive of the fire emitted and a small and variable quantity of phlogisticated air; and when the oils containing the smallest quantity of water were used, the weight of the fixable air equalled or exceeded that of the oil. In burning the inflammable air expelled from acetous acid, the fixable air always greatly exceeded the inflammable air in weight, as will be shewn hereafter; and in all these cases the quantity of fixable air was directly proportionate to the expenditure of pure air.

By these experiments I was thoroughly persuaded that some gravitating matter of pure air contributes to the formation of fixable air, and that every combustible product of acetous acid, contains the acid principle of fixable air as well as phlogiston. As the phlogistic products of acetous acid, when it is decomposed by fire, require no other matter but pure air in order to yield fixable air in consequence of their reciprocal decomposition, and this acid affords nothing but water and fixable air, exclusive of these  
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phlogistic compounds, I could no longer doubt of the existence of the gravitating matter of pure air in acetous acid which yields fixable air; and the induction that acetous acid consists of water, acid, air and phlogiston, seemed to me fully established.

By the abstraction of fixable air, and consequently of the pure air of acetous acid, we deprive the remainder of this acid of every property that characterizes an acid, and by the due agency of air we restore to a considerable part of this same remainder, the decided acid characters of fixable air. Therefore one of the principles of fixable air resides as well in our oil, tinder, coal or inflammable air, as in concentrated vinegar, although it shews no property of an acid until it is combined with air.

Although the phenomena of combustion were inexplicable, they furnish no just argument in contradiction of these inferences concerning acetous compounds and air, since by the experiments of the last Section we find that nitrous acid acting on the oil of the



acetous and supplying pure air, contributes to the formation of fixable air, without the aid of fire or the process of combustion, which has nothing peculiar to it except the illumination; for fire is emitted wherever fixable air is formed from the materials above-mentioned, and is as manifest in its escape from the mixtures which impress us only with the sense of heat, and from which it issues slowly and progressively, as in the combustion in which the same matter, issuing more rapidly, and meeting no dense medium to alter or restrain its motion before it is propagated to our visual organs, excites in us the sense of illumination. Thus I endeavour to express facts to which we must presently have recourse, without involving them in any theoretic interpretation.

This recent knowledge of acetous acid, oily matter, fixable air, and dense inflammable air, opens to us a new prospect of many interesting phenomena, which have perplexed and misled the most ingenious Experimenters. A concise and general explanation

planation of these, according with our interpretation of the phenomena already noticed, will now I hope be acceptable to the reader.

In distillations of the acetous acid alone, no change is produced in it, because there is nothing to facilitate an abstraction of its water, or to detain any of its principles in preference to the others, and because the volatility of this compound of water, acid air, and phlogiston, limits the heat which it sustains in this process. But when the same acetous acid is detained by any body which facilitates the abstraction of its water which serves as the intermedium of the union of the other principles, and in consequence of this detention is duly ignited, the acid principle so far as it meets air, forms fixable air, but meeting phlogiston only, forms with it an inflammable body, which in the circumstances respectively described, appears in the form of oil, tinder, artificial fuel, or of dense inflammable air.

In accounting for the production of fixable air, and of oil and inflammable air,

which in combustion yield fixable air, from the dephlegmated and ignited acetous acid, we furnish an easy explanation of the phenomena which occur in the distillation and combustion of all the vegetable and other substances which yield fixable air, oil, and our inflammable air, in various proportions; and we shew at the same time that however they may vary in their other principles, and consequently in their properties, they all contain our vegetable acid principle associated with phlogiston. The nature of the coaly and charred residue left in the distillation of vegetables and divers combustible mineral substances, is clearly shewn by the like residues of acetous compounds; for so far as all these yield dense inflammable air by mere ignition, or fixable air in combustion, the existence of our acid principle in each of them is manifested.

When we consider that in every dephlegmation of the acetous acid a great deal of oil is formed, and that all oils in their combustion shew, by the quantity of fixable air, that they consist chiefly of our acid principle

principle and phlogiston detained, in some instances, by a little earth or other fixed matter, and associated, in others, with a little water; and when we also observe that waxy, resinous, bituminous, and divers other solid combustible bodies may, by distillation and the abstraction of earthy matter, be reduced to the state of oil; we find sufficient reason to conclude that the form and characters of oil are those which our acid principle and phlogiston, abstracted from other matter, are most disposed to assume; and as no oil or ardent spirit, or resinous or camphorated or coaly substance, exists without them, and nothing else is common to all the bodies that are combustible; I shall for the future express the compound of our acid principle and phlogiston by the term of oily or coaly matter, rather than introduce new terms.

As the most dephlegmated acetous acid sustains certain degrees of heat, and may be distilled without decomposition, for the reasons above-mentioned, we readily conceive how ardent spirits and the purer oily bodies

retain their form and characters after the like treatment, and how camphorous bodies, flowers of Benzoin, and others, consisting chiefly of our oily or coaly matter, may be sublimed unaltered; and for the same reasons that acetous acid duly heated, undergoes the changes already described, ardent spirits, oils, and all the volatile bodies which abound in our oily or coaly matter, are convertible, to the amount of this matter, into inflammable air, when they are detained by any body, or pushed through red hot tubes, in order to undergo the necessary ignition.

A cursory review of the particulars comprehended under these general observations, is sufficient to shew how copiously and extensively our acid principle is diffused through the animal and mineral as well as through the vegetable creation, how constantly it attaches itself either to the gravitating matter of air, or to phlogiston, and why in all our attempts to expel it from fixed bodies, we find it compounded in the form of fixable air, inflammable air, or oil,  
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which last bears the same relation to our acid principle that sulphur has to that of vitriolic acid, or phosphorus of Kunkel to that of the phosphoric acid.

The fixable air, inflammable air and oil, procured in the distillation of wood, peat, bitumens and fossile coal; and the fixable air which is produced abundantly in the combustion of such native substances, or of their oil or inflammable air, shew clearly that these fuels differ from each other only in the quality and quantity of earthy saline and other matter combined in them with the principles of our vegetable oil, which thus appears to be common to them all, and to constitute the greater part of them abstracted from their water. Those who wish to trace mineral fuel to a vegetable origin, will find the characteristic matter of it abounding in all organized bodies on earth, and even in their relicks after rotting, and may observe that black peat strongly compressed, differs very little from mineral coal, either in the appearance, or analysis, or products of combustion: and the circu-



lation of the same oily matter to vegetables again, is exhibited in the practice of husbandry. Virgin mould, however richly impregnated with the matter of the vegetables which have perished on it, is exhausted by the repeated removal of heavy crops, and cannot by any culture or mixture be enriched again for vegetation, without receiving, in some form, our oily matter, which we thus trace into the crops, until the exhausted soil can bear no other than stunted vegetables subsisting chiefly on the nourishment conveyed to them by the air or rain.

The agency of water in vitriolic acid is by all allowed to be the same as we described it in regard to the acetous: hence it happens that water impedes the action of vitriolic acid on all bodies by which it can be phlogisticated, and that vitriolic acid and acetous acid, which however concentrated, contains a great quantity of water, produced little or no effect on each other, when they were mixed in equal quantities. But when the proportion of water in the  
mixture

mixture was lessened by adding only a little of the acetous acid to a great quantity of the most dephlegmated vitriolic acid; and when the acetous acid, detained in the vitriolic, divested of water, and considerably heated at the same time, was deprived of that part of it which issued in the form of fixable air, the remainder then consisting only of phlogiston associated with the vegetable acid principle, was exposed at once to the action of fire and vitriolic acid, which, as we shall presently shew, contains pure air, and always deposits it in the act of combining with phlogiston, to form volatile sulphureous acid. Then whilst the vitriolic acid became phlogisticated, its air acting as usual on the hot oily matter, contributed to the formation of fixable air. But in proportion to the water which yet remained to impede this decomposition, a part of the oleaginous matter escaped in the form of ether or inflammable air, and a portion of the vitriolic acid remained imperfectly phlogisticated.

The action of vitriolic acid on ardent spirits, oils, and all the bodies which contain  
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our oily matter, is of the same kind : for weak spirits are not sensibly affected by this acid, and to produce the greatest alteration in both, we must mix them in their most dephlegmated state. Then the water, which is a constituent part of alcohol, being detained by the vitriolic acid, and some part of the acid principle of the alcohol being expended in the formation of fixable air which escapes, so much of the acid principle of the spirit as can be saturated with its phlogiston to form an oily liquor, passes off in distillation, under the name of ether. This is followed by the water impregnated with some concomitant ethereal and oily matter ; and so much of this last as the vitriolic acid can detain, is afterwards expended in phlogisticating this acid by one of its principles to form volatile vitriolic acid, and contribute by its acid principle to produce the fixable air which accompanies the vitriolic acid air.

In the mean time a part of the oily matter thus heated, escaping the action of the vitriolic, is expelled in the form of inflammable

mable air, to which this oily matter is always convertible by heat alone : and with regard to the thick livid residuary matter, we need only observe that it contains a considerable quantity of vitriolic acid unaltered, and derives its spissitude and colour from the salts of the vitriolic acid and the saccharine matter of the spirit entangling a portion of oil : but as the saccharine matter itself consists chiefly of the acid and phlogistic and aerial principles of acetous acid, the produce from this residue by distillation to dryness, is vitriolic acid, vitriolic air, fixable air, and inflammable air in small and variable quantity, for the reasons already mentioned.

In acetous acid and ardent spirits the acid principle predominates over the phlogistic, and is accompanied with some air ; for otherwise they could not yield fixable air, as they do, in divers processes, without the aid of pure air ; and spirits could not render salt of Tartar mild and crystalizable, as they usually do in digestion or distillation. But in oils, the acid principle appears to be saturated

turated with phlogiston, and the quantity of water which such a compound can retain or unite with is, in all cases, proportionate to the quantity by which our acid principle predominates in the oil; except when some other matter serves like this as the medium of union between the oil and water.

This being the nature of oils, so far as we can briefly express it in general terms, we are next to consider the phenomena which vitriolic acid and oily bodies have been observed to produce.

When diluted vitriolic acid is presented to an oil, they produce little or no effect on each other, for the reasons above-mentioned: but when the dephlegmated acid is used, its first action is to abstract the water and thicken and char the oil. The products are afterwards fixable air, inflammable air, vitriolic air, leaving a coaly residue proportionate to the heterogeneous salts in the acid and the proper earthy or other fixed matter of the respective oils.

To account for these products, we need only make the obvious application of what has been said with regard to vitriolic acid and acetous acid in distillation.

In like manner, the production of fixable and vitriolic air, and all that occurs when we mix or distil vitriolic acid with any vegetable or other substance abounding with our acetous principle and phlogiston, are easily explicable, under due consideration of the matter combined in these substances respectively with our oily matter, and of the predominant acid, in some instances, which with the concomitant air will afford fixable air to which the aerial principle of the vitriolic acid may not yet have contributed.

As to the heat produced, on the mixture of vitriolic acid with oily and other bodies abounding with our acid and phlogistic matter, it is manifestly owing to the capacity of the phlogistic compound and of the vitriolic acid severally to retain more fire combined in their substance, than can be afterwards engaged



engaged as a component principle of the fixable air, vitriolic air, or other product of the process: and that the degree of heat should be proportionate to the expenditure of the air of the vitriolic acid in the formation of fixable air, will not appear singular, when it is considered that in the deflagration of our inflammable air with pure air, fire is most copiously emitted, and nothing remains but fixable air and water, except a small and uncertain quantity of phlogisticated air, as will more fully appear hereafter.

In comparing the inactivity of nitrous and acetous acids on each other, with the phenomena attending the mixtion of nitrous acid with the oil of the acetous, we discover the agency of water in all similar mixtures: for the acetous acid differs from this oil, in nothing that affects the nitrous acid, except water. The elective attractions of the phlogistic and acid principles of the acetous acid, and the aerial and acid principles of the nitrous, the consequent decompositions and new products are therefore sufficiently exhibited

bited in mixtures of this oil with nitrous acid, and serve to explain many phenomena which have occurred to Experimenters in their trials of nitrous acid with bodies containing the acid principle of acetous acid as well as phlogiston.

So far as the principles of our oil and nitrous acid were duly applied to each other, and unrestrained by water, the phlogiston of the former attached itself to the acid principle of the latter, and made nitrous air, whilst the nitrous acid deposited and transferred its air to be expended chiefly in the formation of fixable air : and as the new products could not retain all the fire originally combined in the oil and nitrous acid, a considerable quantity of it necessarily escaping, acted in its proper character, heating and expanding the mixture and the contiguous bodies. But inasmuch as the principles of the oil and acid were accompanied with water, and were restrained by it, or in imperfect mixture eluded each other, we had inflammable air or oily vapour in consequence of the heat, and nitrous vapour or acid partially phlogisticated.

In this manner and even in these terms we can easily account for the products and phenomena of nitrous acid with divers vegetable and animal substances, which contain our acid principle and phlogiston, viz. the heat, the intumescence, the nitrous and fixable air, the escape of inflammable air and oily vapour, and the semi-phlogisticated state of some part of the nitrous acid.

Many experiments admitting or requiring this explanation, may be met in the works of the latest writers on chemical subjects, and particularly in Dr. Priestley's second volume of Experiments and Observations on Airs : but in every exposition of this kind, due care should be taken that the fixable air which the phlogistic body alone may yield, be not confounded with that to which the air of the nitrous acid contributes.

In explaining the phenomena attending the mixture of nitrous acid with bodies consisting chiefly of our oily matter and water, the agency of this last is especially to be considered. The first effect of the nitrous acid  
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in these cases is, like that of the vitriolic, to abstract the water, and then act like diluted nitrous acid on the other matter of these bodies : so nitrous ether is made from spirit of wine and this acid, of which some part remains in the water abstracted from the ethereal or oily matter, another part blends with the ether, when heat is avoided, whilst a portion of the pure or empyreal air is expended in the generation of fixable air ; and proportionate to this expenditure we find nitrous and phlogistic air, the quantities of which are greatest when, by extraordinary dephlegmation of the acid and spirit, or by the heat of hasty mixture, or the want of due compression, the action of these last on each other is rather promoted than moderated.

Substances which consist almost entirely of our oily matter, and afford little or no water to dilute the nitrous acid and moderate its action, produce the greatest quantity of fixable and nitrous air ; which are expelled with such impetuosity as to blow a great part of the ingredients away, before  
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they can be blended sufficiently for their mutual decomposition. This happens in mixtures of nitrous acid and essential oils, which always emit a great quantity of fire, generally burst forth into flame, and burn with great rapidity. When the decomposition is partial or incomplete, the fire emitted is partly waisted away with the elastic fluids newly composed, and partly expended in vaporizing the undecomposed parts of the ingredients; but when neither water nor any other matter gives any considerable impediment, and the circumstances favour the action of such bodies on each other, they are almost wholly expended in forming the new compounds of fireable air, nitrous air, phlogistic air, and water; and the vivid flame and intense heat shew that the fire which was lodged in the oily matter, and in the air of the nitrous acid, is for the greater part liberated to act in its proper character on the neighbouring bodies.

All the phenomena that accompany the action of nitrous acid on other bodies, which like these contribute to the formation of  
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fixable air, are fimilar to, and intermediate between thofe of folutions, of the proceffes for ether, and of the inflammation of oils, and differ from them in nothing that can embarrafs an experienced chemift.

Notwithftanding the attractive power with which nitrous acid is combined in alkalies earths and metals, the force where-with its empyreal air is drawn to the principles of our coaly matter, is always fufficient under due ignition, to produce the effects lately defcribed, and particularly the formation of fixable air and nitrous air, which is often accompanied with a confiderable quantity of phlogiftic air. This laft indeed varies greatly, as the circumftances of the procefs and the fubjects of it are varied ; but does not require immediate attention.

The rapid combuftion and explofive power of compounds, confifting of nitrous falt, well mixed in due proportion with charcoal or any other fubftance confifting chiefly of our acid principle, combined with phlogifton, are neceffary confequences of thofe



attractive forces which tend to the formation of fixable air, nitrous and phlogistic air and water, and to the liberation of the matter of fire. Our recent knowledge of these subjects is chiefly derived from that important discovery of Mr. Cavendish, of the emission of fire and formation of water, from the gravitating matter of empyreal and light inflammable air ; and any person who may hereafter compose a theory of combustion and detonation, will find the chief difficulty to consist in the attempt to shew why a combustible mixture, whether elastic, fluid, or solid, requires ignition in some part before the intended decomposition can take place. My conjectures on this subject will appear in a subsequent section.

A great many different pyrophori are made by mixing earthy, metallic, or alkaline bodies, with vegetable or animal substances consisting chiefly of our oily matter, and then expelling their moisture and superfluous oily or acidulous matter, by ignition in close vessels. Nothing but this oily or

coaly matter is common to all the pyrophori, which by mere exposure to pure air, imbibe it suddenly, enter into combustion, and yield fixable air; which, if it be not copiously emitted during the combustion, is found to be detained in the earth or alkali of the pyrophorus, from which, previous to the admission of air, little or no fixable air could be obtained. The fixable air formed in all instances of this kind, is manifestly the product of the oily or coaly matter, and pure or empyreal air; and the fire liberated and spontaneous accension, shew clearly that one or both of these contained a much greater quantity of fire, than the new products, consisting of fixable air water and residuary gross matter, can retain.

After this manner, we may easily explain the phenomena of fixable air and heat wherever they are produced, during the action of empyreal air, (or atmospheric air which contains it) on substances containing our oily or coaly matter; and the same interpretation is applicable, wherever we see fixable air formed, and fire extricated

during the action of nitrous salts, black wad, or of other bodies containing empyreal air, on combustible bodies holding our oily or coaly matter. But since mixtures of solid bodies containing empyreal air intimately combined in them, with other solid bodies containing our oily matter, emit fire abundantly, and burn most vehemently, so soon as the action of the aerial matter of one, on the oily matter of the other, commences, whether spontaneously, or by the excitation of a flint spark; we cannot doubt that the empyreal air, or oily matter, or both, retain a vast quantity of fire fixed in the solid substance and as much neutralized as acid is in a neutral salt: and in comparing the action of the elastic fluid called empyreal air, in the combustion of phlogistic bodies, with the like effect of nitrous and other solid bodies, which act in combustions by virtue of their pure air, we find no ground for supposing that much more of the matter of fire is necessary to the elastic condition of pure air, than can be retained by it in the closer approximation of its parts, in bodies

to whose mass and weight it greatly contributes; unless we admit, that fire is combined in much greater quantities in phlogistic bodies than in any other; in direct contradiction to the opinion of the ingenious Dr. Crawford, who very justly considered the empyreal air as the vehicle of fixed fire; but will now, on a review of the subject, if I mistake not, admit, that phlogistic bodies also contain fire, and emit it in combustion. But the vivid combustions of *light inflammable* air, sulphur, zinc, and other bodies, with pure air, in which little or no fixable air is formed, as that excellent philosopher Mr. Cavendish has shewn; teach us that fixable air is not a necessary product of combustion, nor of the union of air with phlogiston: And now we see, that it cannot be produced by the union of air with any known matter, except the acid principle manifestly contained and disguised by phlogiston, in the bodies comprehended under the general heads already specified, and consequently in substances whose varieties,

distinguished only by the names, would fill a volume.

The processes of fermentation, putrefaction and respiration, which last, as Dr. Crawford very sagaciously observes, generates animal heat, are all productive of fixable air, of which, a great part is actually formed from principles which before were otherwise engaged and compounded in the respective instruments of these operations; and these processes are all attended, like those above described, with the emission of fire. But as I intend to speak of these subjects elsewhere, I shall not insist on them here for the mere purpose of shewing, what the reader anticipates, their conformity with the notions so often tried in the interpretation of the phenomena which accompany the formation of fixable air in various processes.

The appearance of small quantities of fixable air, in processes which do not rank under any of the forgoing heads, is generally



rally owing to the following circumstances: The common nitrous acid of the shops is distilled from rough nitre, and exclusive of water, carries with it some of the vegetable oily matter, which colours it, and in every circumstance of dephlogmation and ignition, yields fixable air. In the refining of nitre, we approximate the intended purity, but never attain it perfectly; and therefore find some fixable air mixed with the first product of nitre distilled even in glass vessels. The moats also, or dust and fibres, whether animal or vegetable, that are wafted every where in the air, and adhere to our vessels and instruments, never fail to impregnate the subjects of our experiments, and to yield fixable air, when exposed to heat and the action of air or of bodies containing this matter. Coarse earthen vessels generally retain in their substance some of our oily or coaly matter; the imperfect metals are seldom free from it; and a grain is sufficient in the recited circumstances, to produce some cubic inches of fixable air, as will be shewn hereafter. It is not, there-



fore a matter of surprise, that in the inconsiderate use of impure materials, earthen vessels, dirty gun barrels, and by exposure to the common air, many substances should have appeared to yield variable quantities of fixable air, which in the contrary circumstances could have afforded nothing of this kind.

We cannot yet speak with certainty of the character of the mere acid matter of each of the chemical acids, abstracted from phlogiston and every other kind of gravitating matter. In each of the substances, which we consider as a certain acid saturated with phlogiston, the acid matter is as much disguised as it can be in a neutral salt: This appears in the comparison of sulphur with vitriolated tartar, of phosphorus with microsmic salt, of regulus arsenic, with neutral arsenical salt, &c. all which differ very much from their respective acids. But as empyreal air is administered in every process in which we are supposed to dephlogisticate the mere acid matter, and this last is not known to us in the state

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intermediate between that of its combination with phlogiston and this last in which it is certainly combined with gravitating matter of empyreal air, we cannot pretend to describe any mere acid matter in its uncombined state; nor is it yet demonstrated, that the empyreal air, which is a constituent part of each of the acids of the chemists, expells or extricates in every instance, all the phlogistic matter which was formerly combined in the subject from which the acid is prepared. There is, however, in the preparation of every acid, sufficient evidence either of the expulsion of some phlogistic matter, or of its union with the pure acid matter being dissolved in consequence of its being expended in the formation of water, of which a part, or the whole in most instances, is retained in the body which we are said to dephlogistificate.

Whenever vitriolic acid is employed in the formation of sulphur, its empyreal air is expended in forming fixable air or water; the acid character of the residue is lost in  
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the union with phlogiston, and cannot be restored until empyreal air is administered in some shape to combine with the mere acid matter and with a part if not the whole of the phlogiston, which with a portion of the empyreal air forms water.

This agency of empyreal air appears in every process for making vitriolic acid from sulphur and nitrous acid or nitrous salt, or sulphur and empyreal air, whether administered pure, or blended with phlogistic air, as it is in atmospheric air; and the extrication of the empyreal air from the other matter of vitriolic acid, whilst it is employed in the formation of sulphur, is equally apparent in every experiment in which artificial sulphur is formed in considerable quantities, as in making liver of sulphur with charcoal and vitriolated tartar or glaubers salt, or in making pyrophorus with alum and flower or sugar; for in these instances, and in every distillation of vitriolic acid or vitriolic salt with charcoal, coak, bitumens, oils, resins, and divers substances which severally yield little or no fixable  
air

air or water until empyreal air acts on them during ignition, the quantity of fixable air and water produced during the intended formation of sulphur, shews that the proper air of the vitriolic acid, is excluded from the sulphureous compound.

Although vitriolic acid be divested of water in the long continued fusion of Glaubers salt, it obstinately retains the greater part of its empyreal air; and until this is engaged and expended in the formation of fixable air and water, the vitriolic salt cannot make liver of sulphur with charcoal or the other substances that abound with our coaly matter. The agency of this last in the extrication of the empyreal air of Glaubers salt, is the same as in metallic reduction; and the liver of sulphur thus made by fusion, shews how much the acid character of vitriolic acid depends on its empyreal air: For the saline mass now containing almost all the mere acid matter which belonged to the Glaubers salt, but deprived of the air, is no longer neutral and mild, but tastes strongly alkaline and caustic,

tic, and is deliquescent. Exposed to empyreal air it imbibes it greedily, and without meeting any other matter, resumes the characters of Glaubers salts. Vitriolated tartar treated in the same way, affords the same phenomena and inferences.

The nitrous acid, in like manner, loses its acid characters, and acquires those of nitrous air, when it is deprived of the empyreal air, and is supposed to receive phlogiston, in metallic solutions, or in combustions and detonations. When the quantity of nitrous air is considerable, the empyreal air which had been detached from it in such processes, is easily traced in the bodies which effected the separation, as in the nitrated calces, or in the water formed, or in the fixable air; and the nitrous air never resumes the true characters of nitrous acid, until it meets empyreal air, with which it recomposes nitrous acid and its water.

It is not to be denied that in processes of this kind, as well as in the expulsion of empyreal air from nitre, a considerable  
quan-



quantity of phlogistic air appears, of which I cannot yet speak with precision, although I am certain there is nothing in it repugnant to these notions of acids.

Phosphorus of Kunkel, as the celebrated Scheele and Lavoisier have shewn, imbibes empyreal air in great quantity. During its saturation with the air, nothing but fire is perceptibly emitted, and this which has been called dephlogistication, is really effected without any emission of the phlogistic matter, because there is no loss of weight, and water is manifestly formed.

In the phosphorus, the acid matter is totally disguised by the combination with phlogiston ; in the transition to phosphoric acid it may be equally disguised, because it combines with the gravitating matter of empyreal air ; but it is only in this combination with air that it forms a substance possessing the common chemical characters of an acid.



How the mere acid principle of phosphorus would act, if it were perfectly freed from phlogiston and empyreal air, I know not ; but I am assured that the empyreal air is not all expended in forming water with the phlogiston of the phosphorus, and that it does not act merely by dissolving the union between the phlogiston and acid principle, which in the latitude of speech may still be called dephlogistication ; for the astonishing quantity of empyreal air which phosphorus imbibes in combustion, to the amount of about twice its own weight, is not all emitted in the form of water, but serves as well as disengaged empyreal air, for the greater part, to compose fixable air, when the phosphoric acid is formed into phosphorus again, by distilling it with charcoal or other substances containing the acid principle of fixable air.

Arsenical matter combined with phlogiston to form Regulus of arsenic, has more of the character of a combustible metallic substance than of an acid ; and it is only  
by

by absorbing empyreal air in due quantity, that it acquires the general properties of a chemical acid. That this empyreal air is not wholly expended in abstracting the phlogiston, but that it actually contributes to the formation of the acid, may easily be shewn, 1st, by the fixable air which is produced in great quantity during the reduction to the reguline state by such phlogistic substances as contain our oily or coaly matter; 2dly, by the empyreal air which this acid emits when it is strongly ignited and sublimed into the form of white arsenic; and 3dly, by the rapid combustion of zinc fused in this acid, as Mr. Scheele has observed.

In the preparation of the acid of sugar and of other facitious vegetable acids, all the phenomena correspond with these notions of the acids in general, and with no others. The nitrous acid employed in such processes is wholly expended thus: its empyreal air in forming water and the vegetable acid, whilst the remainder of it escapes in the form of nitrous air, if not of

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phlogistic air : The empyreal air thus deposited in the saccharine or other vegetable acid, is demonstrable, in the greater quantity of fixable air that may be expelled by mere ignition from such an acid, than from an equal weight of the sugar or other substance which was formerly supposed to contain such acid disguised only by phlogiston.

We are indebted to the ingenious Mr. Scheele and Mr. Lavoisier for many excellent experiments and observations, which illustrate all that is here advanced concerning the matter of acids and pure air, although their conclusions concerning phlogiston and fixable air are exceptionable, as is the use of the term oxygenous principle ; for as empyreal air is common to many other bodies as well as to the chemical acids, and contributes to the formation of acid, only when it combines with and dephlogisticates some particular kind of matter, the term oxygenous principle is applicable rather to this last than to the empyreal air, and it is only in this latter sense that we want it.

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The marine acid eludes this analogy in no other particular than the stronger adhesion of the empyreal air, which we cannot separate totally from the acid matter by any art yet discovered.

When dephlogisticated marine acid is prepared, by mixing the nitrous with the common marine acid, the change produced in this last, is proportionate to the quantity of nitrous air which is always produced and emitted from the mixture, and consequently to the quantity of pure air which is drawn by the marine acid from the nitrous: thus, dephlogisticated marine acid made in this way, appears to consist of marine acid saturated with empyreal air: and as the menstrual power of every acid is abated by phlogiston, and encreased by the accession of empyreal air; so the fully aerated marine acid becomes a solvent of bodies which resist the ordinary marine acid.

But independent of the intensity which an acid solvent acquires by the accession of air, the nature of metallic salts and calces,

requires that the solvent should supply pure air abundantly ; for, as this air is a necessary constituent principle of such bodies, the transition from metal to salt or calx, can take place only as the menstruum supplies air. Hence the efficacy of nitrous acid in calcining metals, and of the dephlogisticated marine acid in dissolving those which resist the common spirit of salt.

On these considerations, the marine acid does not yet appear as an exception to these notions of the agency of empyreal air in acids ; nor will it afford any stronger objection to them, after the relation of the following phenomenon, which has not, to my knowledge, been noticed by any chemist.

The acid elastic fluid which issues when two pounds of manganese are mixed and distilled with two or three of ordinary spirit of sea salt, may all, except a small portion of phlogistic air, be condensed in a solution of fixed vegetable alkali ; and the  
solution

solution thus impregnated, yields a considerable quantity of nitre, which crystallizes in the ordinary form, and detonates on red hot coals. The solution at the same time yields regenerated sea salt.

It is to be observed, that manganese, by mere ignition, yields a great quantity of empyreal air with phlogistic air, as nitre does; and from these facts I conclude, that manganese contains nitrous acid or the principles of it in great quantity.

But red lead, and the calx which serve to dephlogisticate the marine acid, or to produce the change in it that is expressed by that word, also yield empyreal and phlogistic air by ignition; and I venture to prognosticate, that nitrous acid will also be found in these cases to make aqua regia with marine acid, exclusive of any change producible in the marine acid, by its union with empyreal air supplied from the calx.



Since air then is a constituent principle of all these, and necessary towards their acid character, and since the marine acid affords no contradictory instance, it is perfectly conformable to the tenour of nature, that acetous acid should contain air and possess the acid character, as much by virtue of this air as of any other matter of it; and as the union of a specific matter with phlogiston, makes sulphur, but with air, vitriolic acid; or as the union of a certain kind of matter with phlogiston, makes phosphorus, but with air, phosphoric acid; it is perfectly conformable to the known nature of acids, that the peculiar matter which distinguishes the acetous from other acids, should attract phlogiston, and in this union exhibit none of the acid characters, but appear as an oily or camphorous or resinous substance, bearing strong resemblance, in divers properties, to sulphur or phosphorus, and a weaker similitude only when it is overwhelmed with other matter, as it is in spirits, sugar, gums, vegetables, fossil coal, &c.; and finally that by receiving  
 empyreal

empyrean air, and depositing a part of its phlogiston, it should assume the acid characters that appear in acetous and other vegetable acids and in fixable air.

In speaking of sulphur, the subjects which claimed my chief attention, did not require that I should deviate from the common notion of its being composed of mere acid matter and phlogiston; but it is now expedient to declare that in a great number of experiments it appears to me that sulphur contains a small portion of our oily matter; and it is owing to the prevalence of the vitriolic acid, that the small quantity of fixable air, which is formed during the combustion of sulphur, does not shew itself by the test of lime water presented to the acid vapour.

Inductive reasoning is ever liable to error, but approaches the nearer to be conclusive, as the induction is more general, free from experimental exception, and applicable in the solution of phenomena, which do not appear to be explicable

upon any other general ground. The matter of this section then is to be considered rather as a test and probation of my notions concerning acetous acid, fixable air, oil, and dense inflammable air, than as an attempt towards explaining, in so small a compass, all the phenomena that have been noticed on this occasion.

The terms which have been hitherto used by chemical writers, are in many instances utterly unfit for these discussions, and render them as embarrassing to the writer, as they may be obscure to an inattentive or captious reader. The most correct of our writers have felt this inconvenience; and until the new notions are adopted by general consent, philosophers will rather continue to read with candour and indulgence, than encourage the premature introduction of new terms.

## SECTION XI.

*Experiments and Observations on Acetous Compounds Containing Volatile Alkali; and Reflections on the Varieties Analysis and Products of divers Substances.*

THE new and unexpected appearances which occurred to me in my first experiments on acetated volatile alkali, prompted me to repeat them often on a very large scale, and to vary them so much, that a full detail of all that relates to them cannot be introduced in this essay. I shall however give a summary view of the particulars which seem to be remarkable, either for their novelty or their aptitude to our purpose of tracing the principles and properties of acetous acid.

The water inherent in the concentrated acetous acid and in the rectified volatile alkaline salt of sal ammoniac, is sufficient to keep the neutral salt which they form, in perfect solution. But the neutral li-

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quor shews a considerable degree of tenacity or spissitude, although it be colourless and transparent.

In neutralizing the acid with a caustic volatile alkaline liquor, consisting of six parts of water and one of mere alkali, the heat excited amounts to  $150^{\circ}$ ; and as the alkali used is stronger the heat is greater. The dense white fume which clouds the vessels in which this mixture is made, consists chiefly of neutral salt formed by the union of the acid vapour with the alkaline air which continually issues from the alkaline liquor when it is pressed by the atmosphere only, without any intermediate impervious body.

The uncommon duration of this dense white vapour, or the slow condensation of it into a neutral salt, implies a slow extrication of the proper fixed fire of the acid vapour and alkaline air in consequence of the counteraction of contrary powers. For the parts of the acid and alkali tend to retain their respective portions of fire, though

though not so strongly, as the attraction which draws them into contact, tends to exclude the greater part of it, as it happens in the formation of the neutral salt.

When the acid is neutralized by concrete mild volatile alkaline salt, of which it requires about an equal weight, the mixture is rather cooled than heated in temperate weather; shewing that the fixable air expelled from the alkali, engages and carries off with it, in a state of combination, all the fire which otherwise would shew itself under its proper characters.

In distilling the neutral liquor, the first effect of the heat is to expel a considerable part of the alkali in the caustic and aerial state, and the emission of alkaline air continues until the liquor condensed in the recipient, amounts to one fourth of the bulk of the charge.

This being drawn off and examined is found to consist of water saturated with caustic volatile alkali, and impregnated with



with a part of the neutral salt which passes over along with the watery vapour, and of which the quantity is greatest in quick distillation, but rarely exceeds one eighth of the neutral salt employed.

What follows, is for a moment neutral, but after a few drops, issues strongly acid to the taste, and consists of water, acetic acid and neutral salt, a part of which crystallizes in the acid liquor, in cooling; and the product is of this kind, until the original charge is reduced to about half its bulk.

After this, the matter in the retort becomes neutral, and then concrete and crystalline by cooling: But by slow sublimation it forms long slender flatted crystals terminating in sharp points, shooting from the sides of the vessels in divers directions, irregularly piled on each other, but leaving large interstices, and having no predominance of acid or alkali, to the taste: Their hue is pearly white, and their length seldom

dom exceeds an inch and eight tenths, but is much less in hasty sublimation.

The crystals which form towards the conclusion of the process are not so white as the former, and the last of all are yellow, as if stained with oil. A very thin crust of fixed black matter always remains at the bottom of the retort, adhering firmly to it, and too small in quantity to admit of strict examination.

The white crystals have a peculiar smell, which differs considerably from that of the yellow, which is a little offensive, and not unlike that of the smoke that issues during the combustion of succulent vegetables for potash. Thus the neutral liquor affords first the volatile alkaline odour, then the acid variously modified, then divers gradations in the smell of the neutral sublimate, until it becomes empyreumatic.

When a weak solution of acetated volatile alkali in water, such as may be made with acetous acid and the caustic volatile spirit

spirit of fal ammoniac, is slowly distilled, the volatile alkali arises in greater quantity, in the beginning of the distillation, and requires some water to be presented in the receivers, in order to condense it, until a sufficient quantity of watery vapour issues along with it from the charge. This alkalinized water serves to neutralize the acid liquor which follows it, until the matter remaining in the retort becomes neutral. Although the greater part of the acetated volatile alkaline salt is thus decomposed in distillation with water, yet a considerable share of it may, in this process, be dephlegmated, because it is less volatile than water. But for this purpose the distillation must be very slow; otherwise the difference in volatility is not sufficient to prevent the salt from passing over along with the water.

The whitest crystals, heated again in close vessels, melt and sublime into white crystals like the former, until the charge is reduced to about  $\frac{1}{3}$  or less; then the sublimate shews a yellowish tint, which  
 encreases

encreases to the end, and a black stain is left on the bottom of the retort, but nothing else that merits any consideration in regard to the quantity of the charge.

The yellow crystals sublimed again, afford a white sublimate at first; but towards the middle of the process the crystals last formed incline to yellowness, which encreases gradually in every successive crop. The bottom of the retort shews a stain or film which blackens it, but not any quantity of fixed residue that the tenderest balance could shew in weighing the whole charge.

About this period of the process, the air in the vessels becomes impregnated with fixable air mixed with a small quantity of inflammable air, the cause of which will be considered hereafter.

The same phenomena occur in the fifth, sixth and seventh sublimation of these crystals, by a very gentle and steady heat.

The quantity of alkali predominating in the first product by distillation from the acetated volatile alkaline liquor, is greater as the distillation is more slowly conducted. In this case, that part also which distills with excess of acid is greater; and becomes strong even to causticity about the time when the neutral dephlegmated residue is fit to concrete by cooling: and the portion of neutral salt, which rises along with the alkaline and acid liquors, is, in this circumstance, smaller than it ever is found in quick distillations.

Acetated volatile alkali, in its dry crystalline form, and perfectly purified by five sublimations, melts at the temperature of 170, and sublimes at 250 or thereabouts. It is combustible, very deliquescent, and impresses the tongue first with a sense of coldness and then of sweetness, which is soon followed by the kind of taste that may be given by a mixture of nitre and sugar, in which the sweet is not to predominate over the mawkish taste of nitre.

The last fallow crystals obtained in the sublimation of large quantities of acetated volatile alkali, have a taste not unlike that of sugar made brown and empyreumatic by fusion, are odorous in their driest and coldest state, and smell like the yeast of fermenting melasses.

As the neutral crystals of acetated volatile alkali may be heated and sublimed repeatedly without losing the alkali, and the solution of the same salt undergoes a partial decomposition in distillation, the first product being alkaline, the second acid, and the dephlegmated remainder neutral; water appears to be the chief agent in this decomposition, and to have considerable effect in weakening the union of the acid and alkali:

This acetated volatile alkaline salt copiously precipitates nitrous solution of silver, by virtue of compound affinities, and a considerable predominance of acetous acid will not prevent this effect. This fact demands  
O                      considerable



considerable attention, in the ordinary use of the solution of silver, to detect marine and vitriolic impregnations.

The salt composed of acetous acid and volatile alkali, can not be decomposed by lime as it is represented in Bergman's Tables.

A small portion of lime combines with the salt, and expells a little of that part of its volatile alkali which is so weakly retained in the acetous salt, that it issues, as we have observed, even before the water, in the distillation of solutions of this salt.

Every ounce of the neutral salt combines with a penny-weight of the lime, and the liquor holding a salt of three chemical principles, viz. acetous acid, volatile alkali, and lime, may be evaporated to the consistence of olive oil, without depositing any lime or losing any of the saline ingredients. The taste of the neutral salt is totally altered by this association with lime; and the lime may be recovered by  
precipitation

precipitation with fixed alkali, and will then form felinite with vitriolic acid; so that it undergoes no alteration.

Magnesia operates in a similar manner, with the acetated volatile alkali; and when the salt of three principles, whether holding lime or magnesia, is gradually heated in close vessels, the chief part of the acetated volatile alkali sublimes, white at first and afterwards coloured; but that part which is detained in the earthy matter until it sustains a greater heat, is partially at first, and towards the end totally decomposed, when the heat is increased. The volatile alkali mixes with the oily and watery product, which is similar to that of acetous acid in other experiments; and the quantity of fixable and inflammable air, is proportionate to that of the acid detained, until it sustains that heat which alone is in all cases sufficient for the conversion of acetous acid to water, oil, fixable and inflammable air.

In this treatment of acetated volatile alkali, the smell and taste are incredibly varied, with every change of proportion and of the degree of heat which the principles of it undergo.

The residuary lime or magnesia in such distillations, has all the appearances and properties of the like residues from acetous calcareous salt or acetated magnesia.

The facility with which volatile alkali escapes, in a very weak heat, from acetous acid, when their union is weakened by water, implies that the like decomposition may more easily be effected when the acid is held by matter which attracts it more forcibly than water, and the alkali meets fixable air or other matter, so that the extrication of the acid from the alkali may be effected by compound affinities : and on this ground we may account for the product of volatile alkali in the distillation of mustard, opium, tobacco, and of divers other vegetable substances, whose decoctions and infusions are neutral, and which  
certainly

certainly contain all the principles of acetous acid, because they yield fixable air, inflammable air, and oil in distillation.

The same properties of acetated volatile alkali, and its extreme volatility in distillation coction or sublimation, assists us in explaining the changes which, to the surprise of the ablest chemists, are produced by the coction or distillation of divers vegetables, particularly those arranged in the *Materia Medica* under the head of Antiscorbutics, and lead us to a true analysis which shall exhibit the quantity of this volatile salt or of its principles, as well as that of the earthy watery and fixed saline matter already discovered in vegetable bodies. We see that the purer oily matter of vegetables, consisting of phlogiston and the acid principle of acetous acid, and which spontaneously exhales and diffuses itself in air, maintains a great part of its volatility and odoriferous quality even in conjunction with volatile alkali; and nothing but experiment is wanting to shew volatile alkali, or other matter, acting a

similar part in the composition of the oily sublimates resembling camphor, or ben-zoin flowers, and in the more saline sublimates from vegetable substances, all of which abound with our oily matter.

The appetite of fire which we constantly experience in fixable air, and the consequent facility with which it is expelled from bodies by fire; the like appetite of the phlogistic and acid matter of acetous acid, and the incapacity of even fixed alkalies to retain them under the impression of fire; the escape of acetous acid during the coction of the solution of acetated vegetable alkali; and in a word the recited properties of acetated volatile alkali, point out to us the laws of attraction, or ultimate reason in natural philosophy, by which we are to account for the alkaline, acid, neutral, aerial, and fixed products, so dissimilar in property and quantity, which the very same substances have been found to yield in coction, fermentation, putrefaction, distillation *per se*, and in other processes.

The singular relation of acetous acid to volatile alkali, lime, and magnesian earth, whereby three or more of these may be held in the same salt, is to be considered only as one of many instances of the capacity of this acid to form saline bodies uncommonly compounded, inseparable by the usual arts of crystallisation, and partially or totally convertible by heat. This is to be enumerated amongst the causes which produce that wonderful variety in substances, every one of which abounds with the principles of acetous acid; and it is also to be ranked amongst the impediments to a complete analysis of vegetable bodies.

But although volatile alkali, induces the varieties and appearances lately mentioned in acetous compounds, it is to be observed, that it is not more effectual than water in impeding the conversion of the acetous acid by fire; for so much of the acetated volatile alkali, as is duly ignited in any process, undergoes the same decomposition that happens to other acetous compounds; and nothing has yet been discovered that



can prevent this conversion of the acetous acid by fire.

There is no difficulty, therefore, in accounting for the stain left on the retort in subliming acetated volatile alkali; for the moats and dust which it must necessarily catch from the air, in charging, or from the retort, however clean it may appear, added to the matter abraded from the glass during the operation, and aided by the attraction of the vessel to the salt, are sufficient to detain a small quantity of the acetous compound, until it acquires the heat in which every fixed matter becomes stained with the residuary oily matter of ignited acetous acid. This notion of the phenomenon is supported by the appearance of fixable air mixed with a little inflammable air, at this period of the process.

The varieties of smell and taste which an acetous salt exhibits in consequence of variations in the proportions of its principles, serve to shew, that in the analysis of vegetable and other bodies which differ greatly

in smell, taste, and appearance, we are not to expect as great a difference in the kinds of matter of which they are composed, but are more likely to find in thousands of them, little or nothing more than a certain earth, and alkali, and phlogiston with one or both of the gravitating principles of fixable air. This expression to preclude the consideration of the matter of fire, may be conveniently used, until we find by direct experiment that this matter gravitates.

S E C-

## S E C T I O N XII.

*Preparatory Experiments on red Lead, Lith-  
rage and Lead, and Estimate of the matter  
imbibed or expelled in calcination and re-  
duction.*

WITH a view to the following experi-  
ments with calces of lead and acetous  
acid, I made very accurate assays of lith-  
rage and red lead, the particulars of  
which I omit, as it will be sufficient for my  
present purpose to state the following  
facts.

The ordinary red lead of our manufacto-  
ries, must be slowly dried in a heat not ex-  
ceeding 150 degrees, before the weight  
can be ascertained with accuracy. After  
this the quantity of water that can be ob-  
tained from it in a greater heat is very in-  
considerable, even when the heat is suffici-  
ent to expel some of the fixable, phlogistic,  
andempyrean air of this calx. For experimen-  
tal use, it is therefore sufficient to expose it  
in

in thin strata to the heat above mentioned for five or six hours ; but then it ought to be sifted through a fine lawn sieve, in order to separate the half calcined lead that is generally to be found in it ; because, some particles of the metal, during the calcination, incrust themselves with the calx, and escape the action of the air, and the sparks and coal dust blown from the fire, fall on the red lead during the process, and revive it superficially wherever they meet it duly heated. For this reason the quantity of lead found in the best assays of ordinary minium is variable, and is always greater than that which the same red leads affords, after it has been duly separated from the uncalcined part.

7680 grains, or 16 ounces of red lead, yield 6835.2 grains of lead in reduction; and therefore 844.8 grains are, in this transition, expended in the aerial and aqueous products of the process ; provided the reduction is effected by the mere abstraction of the matter which was imbibed during the calcination, and does not require any supply of phlo-

ston towards the vivid lead. But if any of the phlogiston employed in the revival, is imbibed by the metallic earth and retained in the lead, then the quantity of aerial and watery matter expelled from 7680 grains of minimum must exceed 844. 8 grains, by this quantity of phlogiston. Whether any, or what quantity of phlogiston is expelled in the calcination of lead, is a question which cannot yet be answered with precision. According to the opinion of Mr. Lavoisier, who doubts of the existence of phlogiston, the calcination is effected by the mere entry, and combination of empyreal air with the whole matter of the lead, and the reduction must then be considered as the result of the mere abstraction of this air. Mr. Kirvan, and most other able philosophers, incline to the opinion that the greater part, though not the whole of the phlogiston, is expelled in the calcination, and must be supplied again from a phlogistic substance during the reduction.

After due consideration of the facts on which these different opinions have been founded,

founded, and of my own experiments, I am persuaded that there is no good reason for doubting the existence of phlogiston in this and other calcinable metals: but contrary to the opinion which I had entertained for many years, I am forced to adopt a new motion, that the air imbibed during the calcination of lead, unites with the phlogistic and earthly matter, but expells little or none of the former, and that little or none of the phlogiston used in the reduction of minium, enters into, or contributes to the weight of the lead, but that it is almost wholly expended in combining with the pure air of the calx and facilitating the expulsion of it.

Mr. Cavendish's experiments shew, that the gravitating matter of light inflammable air is phlogiston; and the elasticity of this fluid, as well as the fire emitted during the union of its gravitating matter with empyreal air to form water, shew its affinities to fire and empyreal air, and its aptitude to render those bodies combustible, that hold it in combination. But as lead, like other metals, is combustible, though  
not



not in so high a degree as zinc, and as it yields inflammable air in solution, though not so copiously as zinc or iron, it manifestly contains phlogiston.

In the calcination of mercury in contact with emp.<sup>r</sup> air, the latter is imbibed to a quantity equal to  $\frac{1}{8}$  of the weight of the mercury, as Mr. Lavoisier has shewn; but during the calcination nothing is emitted, and by the expulsion of the emp. air, and without any aid of phlogistic matter, the mercury recovers its former metallic condition. Mercury in these experiments, and the noble metals in others, are found capable of imbibing air and becoming californ without losing any phlogiston; and all the appearances that have been thought to indicate the expulsion of phlogiston, during the solution of mercury and of the perfect metals, are fallacious, since we know that the abstraction of the pure air from the acid employed, leaves the remainder of it in that state which we have been used to call phlogistic, if not truly phlogisticated.

Lead diffused in quick-silver, was found by Dr. Priestly to phlogisticate atmospheric air, and this is now known to imply that the lead imbibed empyreal air. Lead thus deprived of its aggregation, as it is in fusion, and freely exposed to pure air by agitation, becomes calciform whilst it imbibes the air, but emits nothing that glass can retain, and consequently nothing of the phlogistic kind.

Omitting other analogies and arguments, I am now to observe that I have frequently endeavoured to calcine lead in contact with pure empyreal air, and to trace the phlogiston which is generally supposed to be expelled. But insurmountable difficulties attended every attempt, and this one particularly, that the calx first formed precluded the air from the melted lead. So far however as the experiment succeeded, I found an absorption of air, but no emission of any thing like inflammable air, nor of any notable quantity of water, which was indeed the expected product.

The freer and more rapid combustion of zinc, indicates a greater quantity of phlogiston

giston than is held in lead; and yet in burning zinc with pure air, I could never discover, by any water separable from the calx, that its phlogiston was disengaged or expelled.

I do not depend on the accuracy of these experiments, so far as to affirm that no water is formed during the calculations of lead or of other metals, and that none of the phlogiston is detached in consequence of the formation of water; and I am aware, that in the calcination of those metals, particularly iron, which contain some of our oily matter, some fixable air is formed. But since we are not authorised by general analogy to suppose that lead loses any notable quantity of its phlogiston by the calcination, since even in solution it yields very little inflammable air; since it does not detonate with nitre; and yet in the experiments above mentioned certainly imbibe air without yielding any quantity of phlogistic matter or water that might deserve notice in the following experiments; I shall

shall not hesitate in assuming the lead of 7680 grains of minium at 6835, 2' grains, and the other matter at 844, 8 grains : and I may on the same grounds consider the reduction as effected by the mere expulsion of aerial matter, without inducing any considerable error in the following estimations.

Dr. Priestley has shewn that lead exposed to the heat necessary for its compleat fusion, becomes lithrage in consequence of the emission of a certain quantity of fixable air and of purer respirable air than that of the atmosphere. We now express the fact in other words and say, in the transition to lithrage, red lead yields fixable air and empyreal air mixed with phlogistic air in quantities which vary in the successive portions.

As the relative quantity of fixable air is greatest at the commencement of the process, and gradually becomes less as that of the empyreal air encreases ; and as this and other metallic calces are always found

to hold empyreal air more obstinately than fixable or phlogistic air, under ignition, we may safely conclude that well fused lithrage retains as much, or very nearly as much empyreal air along with a small quantity of phlogistic air, as it exceeds its proper lead in weight.

By the assay I find that 7680 grains of lithrage yield 6924 of lead; and for the reasons above mentioned, this quantity of lead, together with 756 grains of empyreal and phlogistic air are sufficient to compose 7680 grains of lithrage. According to this proportion, 6835. 2 grains of lead belong to 7581. 5 of Lithrage, as well as to 7680 grains of red lead, which has been found to contain this quantity of lead; and therefore the quantity by which 7680 grains of red lead exceed 7581. 5 grains of lithrage, in both of which the weight of lead is the same, is the quantity of aerial matter which is acquired in the transaction of the lithrage to red lead, or of that which is expelled by fusing the red lead until it becomes lithrage, viz. 98. 5 grains, grains, of which I find

24. or less to be fixable air, and about 74.5 to consist of empyreal air mixed with the phlogistic.

Before I dismiss this subject I must observe that lithrage by due calcination forms red lead, and that I have seen this process conducted on the great scale of a manufactory. I also can affirm from experience, that by distillation in glass vessels, we cannot discover all that red lead emits during the fusion and transition into the form of lithrage, because the vessel is always corroded and perforated, before the central parts of the charge can be completely melted. When an earthen retort is used, the red lead corrodes it and expels some aerial matter from it, and the part of the lithrage which insinuates itself into the pores of the vessel, being heated more than the rest of the charge, and employed in vitrification, loses some of the proper air of lithrage. In trials of this kind, the quantity of aerial matter expelled during the fusion of red lead into lithrage, is much greater than in the former, and exceeds that which



we have stated by estimation from the best assays.

On due consideration of the nature of acids, and of the agency of empyreal air in metallic solutions and salts, and of the capacity of Phosphorus to imbibe empyreal air; the experiments of Mr. Sage for the revival of metals from diluted solutions by phosphorus, will be found to exhibit nothing repugnant to those notions, although he gives a different interpretation of the phenomena. On the contrary we may discover in these precipitations the strictest conformity with our doctrine, since those are the most conspicuous and compleat, that are effected in the solutions of the perfect metals which lose no phlogiston by solution, or in the solutions of imperfect metals which yield the smallest quantity of inflammable air or phlogiston in solution. Mr. Pelletier's experiment for precipitating reguline arsenic from the solution of acid of arsenic, by passing inflammable air through it, shews the agency of phlogiston and empyreal air in the humid way, but does not prove that the privation  
of

of the phlogiston reduces arsenic to an acid, or that the addition of fresh phlogiston is necessary to restore the arsenic to the reguline state; much less does it serve to shew that lead in calcination loses its phlogiston, or that calx of lead must imbibe and retain the phlogiston of a reducing flux, before it can form lead.

In like manner Dr. Priestly's ingenious experiment for reviving the calx of lead by light inflammable air, does not prove that any of the inflammable air unites with the lead, but shews that the phlogiston of the inflammable air, serves to extricate the empyreal air of the calx; and from the experiments of Mr. Cavendish on empyreal and inflammable air, as well as those which follow, this extrication seems to be effected by the conversion of the empyreal air into water, by means of the phlogistic matter of the inflammable air.

I mention these particulars in order to excite chemists to a revision of the phenomena on which the doctrine of phlogistication and dephlogistication of metals has been

founded, and to caution them against a precipitate condemnation of the notion that lead loses little or no phlogiston in calcination, and that its calx imbibes as little from any phlogistic body during the reduction. If it were necessary to the purposes of our present enquiry that I should express my opinion, all that happens to lead during the calcination and reduction, I should say, the empyreal air imbibed in calcination, is retained along with the proper phlogiston of lead, in a state approaching to that of water, in the calx; and when bodies which can engage this empyreal air, and form it into water or fixable air, are duly administered, it is detached, and leaves the proper phlogiston of the lead to be retained in its former state of combination. But if this is not strictly true in regard to the whole of the phlogiston of lead, it approximates the truth sufficiently for every purpose of our present enquiry.

## S E C T I O N XIII.

*Distillation of two pounds of red lead with half a pound of acetated vegetable alkali.*

**H**AVING found by former experiments that concentrated acetous acid, whether directly mixed with a triple or quadruple quantity of lithrage or red lead, or applied to these by mixing the acetated vegetable alkali with them, revived the whole of the lead, and yielded at the same time a great quantity of dense inflammable air along with the fixable; and wishing to know, first, the result of trials with smaller quantities of the acetous acid, and then the smallest quantity with which the reduction can be effected without waste of inflammable air or phlogistic matter, I proceeded as follows.

Two pounds averdupoise = 13999 grains of sifted red lead and half a pound, = 3499.75 of my driest acetated vegetable alkali, were ground together, and distilled in a Chelsea retort. A more compact vessel was not necessary, because I did not intend to measure the water, nor aim at any great accuracy

racy in regard to the quantity of elastic fluids. The measures in which these were received from the neck of the retort which was lengthened with a slender glass tube, contained each 8.5 cubic inches, and the quantity of atmospheric air included in the neck of the retort and glass tube, was so small as not to be regarded in so great a charge. The following table exhibits the measured bulks of the recent elastic fluids expelled during the process. The first column shews what measures were actually examined; the second represents the number of cubic inches of elastic fluid emitted at any period after the preceeding measure had been examined: the third shews the bulk of fixable air contained in the corresponding measure of the mixed airs, and the fourth shews the cubic inches of phlogistic and inflammable air which issued along with the corresponding quantity of fixable air. It is to be observed however, that the two last columns are formed on the supposition that the proportions of the elastic fluids to each other in the measures which were examined, did not differ much from those of the intermediate portions which were not tried.

measure

<i>Measures.</i>	<i>cub. in.</i>	<i>cub. in. of fix. air.</i>	<i>Cub. inches of inflammable and phlogistic air,</i>
First 3	= 25.5	contained 6	19.5 inflammable air with some phlogistic
the 5th	= 17	8	9 inflammable with some phlogistic.
10th	= 42.5	21	21.5 inflammable with some phlogistic.
20th	= 85	42	43
40th	= 170	85	85
100th	= 510	255	255
120th	= 170	113	57 inflammable air with some phlogistic air,
180th	= 510	340	170
250th	= 595	396	199
300th	= 425	282	143
350th	= 425	282	143 inflammable with less phlogistic air
400th	= 425	212	213 inflammable with still less phlogistic air

These last portions issued slowly, and the retort was now heated to redness throughout.

450th	425	212	213 inflammable air with more phlogistic
455th	42.5	21.5	21 almost all phlogistic, and issuing very slowly
460th	42.5	28.5	14 almost all phlogistic, issuing very slowly

The heat of the charge was now sufficient to compleat the reduction of red lead

465th	42.5	30.5	12 all phlogistic, issuing quicker
470th	42.5	33.5	9 all phlogistic, issuing slow
475th	42.5	34.5	8 all phlogistic, issuing very slowly.

Total 475 4037.5 2402.5 1635

Some watery vapour issued at every period of the process, exclusive of that which was quickly distilled at the commencement from the acetous salt; and of the mixed inflammable and phlogistic airs, about 200 cubic inches were phlogistic, and 1435 inflammable air,





When I had thus expelled 475 measures or 4037. 5 cubic inches of elastic fluid, and could obtain no more by a heat sufficient for the compleat reduction of red lead, and continued for more than 15 minutes, I quickly drew away the fire, in order to prevent the waste of lead or erosion of the retort. When all was cooled, I found the alkali of the acetous salt lying over the lead, and tasting caustic, but yet containing 174 grains of fixable air, and perhaps a little of the matter of the retort which the lithrage might have corroded before it was revived. The lead which formed a mass at the bottom, together with the globules that adhered to the sides of the retort and could be collected, weighed 12439 grains; but as the lead ought to have weighed 12459. 1 according to former experiments, the small particles that could not be detached and collected, weighed about 20 grains.

The lead of the minium employed in this experiment, being 12459. 1 grains, the whole of the aerial matter of the red lead was 1539. 9; and allowing 43 grains  
for

for fixable air, and 30 at the utmost for phlogistic air, for reasons which will appear hereafter, the empyreal air of the minium amounted to 1466. 9 grains. The fixable air of the measures which were examined, was necessarily imbibed into lime liquor, and thus measured before it had cooled to the mean temperature, at which it would measure less by a seventh, and weigh 1043. 372 grains. This and 174 grains retained in the alkaline salt make 1217. 372 grains of fixable air, to which the red lead alone contributed 43 grains; and thus the product of fixable air, from the acetous salt and empyreal air of the red lead, appears to be 1174. 372 grains.

The art of measuring the phlogistic air that was mixed with the inflammable air will be shewn hereafter; here I am only to observe, that the utmost weight of the phlogistic air of this experiment did not exceed 37. 7 grains, of which the minium alone might have yielded 30 grains, and the acetous salt furnished the remainder.

The

The 1535 cubic inches of inflammable air were not of the heaviest kind; but at a medium of the heavy which issued first and the lighter which was last expelled, the whole weighed about 300 grains.

In the acetous salt employed, the acid and water amounted to 1739. 396 grains, and the utmost quantity of acid, abstracted from water, was scarcely 869. 698 grains. But of this quantity 7. 7 grains were of phlogisticated air and 300 grains were expended in making inflammable air, and only 561. 998 grains contributed to the formation of 1174. 372 grains of fixable air produced from the the acid, and the empyreal air of the red lead.

As the experiment and mensuration could not, for the foregoing reasons, go further than to approximate the truth, I contented myself with the following inferences.

As the quantity of the acid which contributed to the formation of fixable air, scarcely amounted to 561. 9 grains, and the quantity of fixable air produced from this  
and

and the empyreal air of the red lead, was 1174. 3 grains, this last air must have entered into the composition of the fixable air and formed one half of its mass and weight, or a great deal more. But since the portion of acid thus expended, could yield, by mere ignition and without the acid of the empyreal air of the red lead, a great quantity of fixable air, by reason of the empyreal air which is a constituent principle of acetous acid; the empyreal air must have made near  $\frac{2}{3}$  of the weight of the fixable air found to have been formed of the mere acid and the empyreal air of the red lead.

As the gravitating matter of empyreal air makes about  $\frac{2}{3}$  of the weight of the fixable air, and as 1466. 9 grains of empyreal air could not have been expended in making 1174. 3 grains of fixable air, of which a part is certainly derived from the mere acetous acid; and as none of the empyreal air issued unaltered, and the whole of it was expended in forming new compounds; a considerable part of it must have been employed in  
the

the formation of water, which issued in vapour at every period of the process.

In this water we trace, in conformity to the experiments of Mr. Cavendish, the phlogiston of that part of the acetous acid which was expended in the fixable air; and then infer that phlogiston is not a necessary constituent principle of fixable air.

Finally, since there was a great surplus of inflammable air, but none of empyreal air, it is certain that the quantity of acid employed could have reduced much more red lead, and engaging more empyreal air, could have assisted in forming a much greater quantity of fixable air and water.



## SECTION XIV.

*Distillation of eight ounces of lithrage, with two of acetous acid previously dephlogisticated considerably by vitriolic acid; and formation of fixable air, from acetous acid and empyreal air, without ignition.*

**B**Y repeated digestions and distillations of acetous acid, from oil of vitriol, I endeavoured to divest it of superfluous oil or phlogistic matter, as far as might be done without decomposing the acid totally. Eight ounces averdupoise = 3499.75 grains of lithrage were ground with four of water, and two ounces = 874.94 of this acid were gradually added.

A slight intumescence ensued, and some acid vapour and elastic fluid escaped; but this last was chiefly the interstitial atmospheric air of the powdered lithrage, and the quantity of the former was too small to be regarded on this occasion. The heat did  
not

not exceed 96 degrees; for the acid was added in successive portions, and much weakened by the water previously mixed with the lithrage.

In the course of two hours, during which the mixture was frequently agitated and ground in a porcelain mortar of Mr. Wedgwood's excellent manufacture, the lithrage became white, and indeed formed white-lead. A Wedgwood retort, which could retain elastic fluids, or any charge, better than the common Chelsea retorts, was charged with the mixture, so that none of it was left adhering to the neck; and my apparatus for saving the condensible vapour and the elastic fluids, being fitted to it, the distillation was carefully conducted, but at the same time as quickly as the mensuration of the elastic fluids would permit.

When the atmospheric air included in the retort and receivers, was almost all expelled, along with the four ounces of water used in the mixture, the subsequent products were measured thus.

cub.

carb. in.	fixable.	phlogistic
first 8	4	4 —————
next 8	6	2 —————
8	7	1 —————
16	15	1 phlog. and inflam.
16	15	1 —————
16	15	1 —————
16	15.2	8 —————
16	15.2	8 inflammable with
16	15.2	8 some phlogistic.
16	15.2	8 —————
8	7.6	4 —————
80	75.6	4.4 —————
80	75.6	4.4 —————
80	75.6	4.4 —————
80	77.8	2.2 —————
80	77.8	2.2 inflam. with
80	77.8	2.2 very little of the
80	77.8	2.2 phlogistic.
80	75.6	4.4 —————
80	75.6	4.4 —————
80	71.2	8.8 all inflam.
80	71.2	8.8 —————
40	35.6	4.4 —————
—————	—————	—————
total 1064	997	66.4 —————

The

The last portions issued very slowly, and the emission ceased when the charge was heated sufficiently for the reduction of lith-rage; and in the middle and latter measures, the elastic fluids carried with them some aqueous vapour.

Neither the first, nor any subsequent portion of the water collected during this distillation, shewed any sign of acid; but it was strongly impregnated with ethereal oil of acetous acid, some of which floated distinct on it, and some was expended in greasing the Recipients. By a trial to be related hereafter, I found that the quantity of oil was not less than 10 grains.

The quantity of water was greater than was employed in the experiment, including that of the acid; but the encrease was not measured, because an earthen retort admits of no accuracy in this particular, unless it be of true porcelain well glazed.

On opening the retort, a large mass of lead was found at the bottom, which with the globules collected from the fumes, weighed

Q                      3125 grains;

3125 grains; and from the appearance of the smaller globules which I could not detach without waste, it was manifest that the whole of the lead was revived, and that if there had been no waste, it would have weighed 3155. 242 grains, which is the whole quantity of lead obtainable from the 3499. 75 of lithrage; the aerial matter of which amounts to 344. 506 grains. By firing the mixture of inflammable and phlogistic air, with as much empyreal air as was barely sufficient for the combustion of the inflammable part, and measuring the bulk of the residuary phlogistic air, I found that the 66. 4 cubic inches of the mixed airs consisted of 20 of phlogistic air and 46. 4 of inflammable air.

Deducting 7. 54 grains which is the weight of the 20 cubic inches of phlogistic air, from 344. 506 the weight of all the aerial matter of the lithrage, we find the empyreal air of the lithrage to be 336. 966 grs.

Of the inflammable air which issued at the commencement of the process, a cubic inch weighed 260; but a cubic inch

of that which was last expelled by the greater heat, weighed less than 2. grs. and by the noticed decrease of the spec. gravity, I was assured that the mean weight of 23 grains in a cubic inch might be assumed in computation, and that the 46. 4 cubic inches weighed 10. 672.

The inflammable and phlogistic airs were measured at the due temperature; but the fixable air, being measured as it issued warm from the extremity of the recipient, contracted in cooling to the mean temperature, by one fifth of its bulk, and in this last state would weigh 454. 632 grains.

According to Mr. Kirvans estimation; the mere acid is to the concomitant water of concentrated acetous acid, nearly as 19. to 49: But I have reason think we are less liable to error in stating them as 20 to 48; and by this rule, the acid employed, amounting to 874. 94, contained of mere acid and its phlogiston 257. 335 grains, and of water 617. 604 grains.



As the inflammable air and oil were derived from the acetous acid alone, and weighed 20. 672 grains, the quantity of the mere acid otherwise expended was 236. 663 grains.

The phlogistic air inflammable air and oil being thus accounted for, the empyreal air of the lithrage, weighing 336. 966, with 236. 663 of the acetous acid abstracted from water, were expended in the formation of 454. 632 grains of fixable air, and a quantity of water not ascertained by direct mensuration, but which must be nearly 118. 997 grains, because this and the fixable air make the weight of the empyreal air and efficient acid last mentioned.

Now it is to be considered that the acetous acid, when by mere ignition a part of it is converted into inflammable air and oil, yields a great quantity of fixable air, which for the reasons formerly stated, is proportionate to the quantity of empyreal air which the acid contained. In this case, the quantity of fixable air producible from the mere acid,

acid, by heat alone, is not less than one third of its weight ; and therefore, without any aid of the empyreal air of the lithrage, the whole of the acid employed in the experiment, may be said to have yielded out of its proper matter 85. 778 grains of fixable air, and the quantity of this last which was not merely extricated, but formed with the assistance of the empyreal air, was about 368. 854 grains; for this with the last mentioned proper fixable air of the acetous acid, makes the whole of the fixable air obtained.

Deducting the inflammable air and oil, the quantity of the mere acid otherwise expended, appears to be 236. 663 grains ; and deducting from this the proper fixable air of the acetous acid 85. 778 grains, we find the quantity of the mere acetous acid, which was expended in the formation of fixable air with empyreal air, and in the formation of water and revival of the metal, to be 150. 885 grains. Thus it appeared that the utmost quantity of acid matter

Q<sub>3</sub>

derived

derived from the acetous acid, in 368. 854 grains of the fixable air did not amount to 150. 885 grains, but fell short of this weight by as much as the proper fixable air of the acid exceeded 85.77 grains, and by the whole quantity of phlogiston expended in the formation of water. Deducting this phlogistic matter, which could not be less than 17 grains, the acid matter in 368. 854 grains of the fixable air, did not amount to 133.885 grains. Hence it was inferred that when the acid matter of acetous acid is employed *in excessive quantity* to form fixable air with the empyreal air of lithrage, the fixable air may consist of a little more than one part of the acid matter combined with two of the empyreal air. By a more accurate estimate of the fixable air taken at 85 grains, it is most probable that the proportions would be found to be accurately two to one, provided fixable air, like other acids, may not subsist with various proportions of the empyreal air.

In this view of the subject, I could not perceive that the lithrage imbibed any considerable quantity of phlogistic matter from  
the

the acid employed; for admitting that in the fixable air formed, the quantity of matter derived from the acetous acid, was no more than one third of the weight of that fixable air, and consequently only 122 grains instead of 133 as it was stated; no more than 11 grains of the acid employed remain unaccounted for; and it is by no means probable that the phlogistic matter appertaining this quantity, could have produced any considerable effect on eight ounces = 3499.75 grains of calx of lead, if it had been really dephlogisticated during the calcination. It was therefore inferred that lead loses little or none of its phlogiston in calcination, and imbibes none during the reduction; but that in this latter process, the calx of lead is divested of the empyreal air together with the small portion of phlogistic air which it imbibes in the calcination.

From some of the phenomena of this experiment, I suspected that the acetous acid could be totally converted into fixable air and water, by combining with empyreal

air, and without the assistance of fire. I therefore triturated this acid diluted with a quadruple quantity of water, with lithrage in various proportions; and found that the quantity of mere acid that was barely sufficient, by frequent trituration, to make the lithrage look white in the course of two days, united with the empyreal air of the lithrage, and in the new forms of fixable air and water, formed with the lead a calciform mass, which after being duly dried and powdered, yielded no acetous acid either in distillation or in solution in vitriolic acid, but afforded fixable air in abundance, and mixed only with a very small quantity of inflammable air.

The weight of the fixable air was always twice greater than that of the mere acid abstracted from water; and in some experiments it was still greater. Thus it appeared that fixable air may be made of its constituent principles, without the aid of ignition, when they meet unrestrained by any counteracting power; and that when  
acetous

acetous vapour or dense inflammable air meet empyreal air without forming fixable air, the counteracting agent is no other than the matter of fire, which causes the repulsion of their parts, and consequently the elasticity of these fluids.

S E C-



## S E C T I O N XV.

*Reduction of lithrage and red lead by acetous acid, and the products.*

**T**O prevent the waste of acetous acid during its action on lithrage, I poured two ounces troy = 960 grains of the strongest concentrated vinegar recently procured from acetated vegetable alkali and retaining all its phlogiston, into four ounces = 1920 grains of distilled water and adding this gradually to 14 ounces = 6720 grains of lithrage, I ground them together. The heat of the mixture did not exceed seventy degrees, and little or nothing was emitted, except the interstitial air of the lithrage powder, which caused a slight intumescence.

The mixture was at first quite soft; but after being ground for about half an hour in a porcelain mortar, it grew stiff, and in two hours it was sufficiently dry to be cut  
into

into slices which were rather friable than plastic. The water then seemed to have been engaged in the saline mass, as the proper water of its crystals.

Having observed in former experiments that this acid required a good deal of time to combine intimately with the lithrage and to form a mass resembling white-lead in colour, I left it closely covered for 24 hours, and then found it so hard and dry as to require some force in cutting out that part which had not formerly been loosened from the mortar. The whiteness which appeared in the superficial parts on the first action of the acid, gradually improved as the mass dried, and at last was almost equal to that of white-lead, with scarcely any appearance of the lithrage colour. It was then distilled in a Wedgwood retort, and the products being measured and examined at shorter intervals than those expressed in former experiments, were stated thus.

The fixable air weighed	658	grains
The phlogistic air	20	
The inflammable	3	

No

No oil appeared in this experiment, and the quantity of water was not ascertained, because in the quick emission of the elastic fluids a great quantity of the watery vapour was waisted along with them, and more was condensed in the measures than remained in the recipient.

In the revival of lithrage by means of acetous acid, charcoal, and other substances, I had repeatedly observed that the quantity of phlogistic air was not as that of the phlogistic matter employed, but as the quantity of the calx reduced to lead, and concluded that the phlogistic air proceeded from the lithrage chiefly. By experiments of this kind I am now persuaded that in the calcination or scorification of lead, the calx imbibes not only the empyreal air, but some part of the phlogistic air of the atmosphere, and that the quantity of this last varies in different parcels of lithrage, from ten grains in 16 ounces to 20 or more, which last was the quantity in this distillation.

In

In the retort I found a mass of lead covered with small grains and globules of the same metal, without any perceptible admixture of unreduced lithrage, all together weighing 6034. 5 grains. The lead which adhered in thin plates and small globules to the sides of the retort, and could not easily be detached or weighed, was estimated at 24 grains; because this quantity with the former makes 6058. 5 grains, the proper lead of the 14 ounces of lithrage.

By the rule formerly established the aerial matter discharged during the reduction of 14 ounces of lithrage, amounted to 661. 5 grains; and as 20 of this quantity consisted of phlogistic air, the empyreal air weighed 141. 4 grains. But as none of this escaped unaltered, it must all have been expended in the formation of fixable air and water; and as none of the acetous acid escaped unaltered, that part of it which was not necessary towards the formation of water, was expended in the fixable air; and the greater part, if not all the phlogiston of the

acetous

acetous acid, except that of the inflammable air which escaped, appears to have been employed in the formation of water. As this acetous acid was of the strongest kind, and neither aerated nor deprived of any oily matter by distillation with vitriolic acid we cannot, consistently with the experiment of the last section, estimate the quantity of mere acid and phlogistic matter at less than 293 grains, or the water at more than 667. But as three grains of the former were expended in inflammable air which escaped the lithrage, 290 grains of mere acid and 641. 5 grains of empyreal air were expended in the formation of 658 grains of fixable air, and of water whose quantity was 273, provided no part of the phlogistic matter of the acid entered into the lead.

This quantity of water required 39 grains of phlogiston, which is almost a seventh part of the acid; and about one fourth of that part of the acid which forms inflammable air by mere ignition: and in this view of the subject we find no reason for supposing that any of the phlogiston of the acid entered the lead or fixable air, or that

it was otherwise expended than in the formation of water.

If the quantity of water amounted to 273, not less than 234 grains of empyreal air, were expended in the formation of it, and the remainder of the empyreal air, viz. 407. 5 grains, was employed in the formation of fixable air, the quantity of which would be 611. 2 grains, provided the empyreal air be to the other matter of fixable air as two to one. But the whole of the fixable air produced was 658 grains, if not more; and this excess is to be imputed to the fixable air which the acetous acid alone is capable of producing when ignited, by reason of that empyreal air which is a constituent principle of this as well as of other acids.

In the hasty distillation of recent mixtures of lithrage and acetous acid, I have often had a greater waste by the escape of inflammable air, and some part of the lithrage remaining unreduced, whether the quantity of acetous acid was greater or less than



than is here represented; and in repeated experiments I have observed that the intended expenditure of the acid, was best effected, by sinking the bottom of the retort an inch or two in the sand-bed of a reverberatory furnace, and thus causing the fire to act from above downwards.

Having mixed concentrated acetous acid duly diluted with water, with red lead in various proportions, and heated these mixtures in the manner already described, I found the products and phenomena to differ from those lately mentioned in nothing but what might have been expected from the greater quantity of phlogistic and empyreal air contained in red lead with the portion of fixable air already noticed.

The quantity of inflammable air was smallest when the weight of the red lead was to that of the acid as 16 to 2, and then did not exceed five grains. The greatest quantity of lead reduced by two ounces of the acid did not exceed eleven ounces and a quarter; and whenever more red lead

was

was used than the acid could reduce, the superfluous part formed lithrage by the fusion, and emitted the quantity of fixable phlogistic and empyreal airs which it usually yields in the transition to lithrage, as we have stated in the 12th section.

In these experiments it always appeared that much more acid was necessary towards the revival of a given weight of lead from red lead, than was required in precipitating the same quantity from lithrage: and as the calx which contained most air and least lead, required the greater quantity of acid for its reduction, I had this additional ground for the opinion that the acetous acid acts rather by facilitating the expulsion of aerial matter from such calces, than by contributing any thing considerable towards the mass or weight of the revived lead.

It is scarcely to be doubted that this doctrine is applicable in other metallic reductions effected by fuel or substances containing our oily or coaly matter; and that the

R

quantity

quantity of empyreal air in any calx, may be determined by the quantity of fixable air and water emitted during the fusion with fuel previously divested of fixable air and water.

## S E C T I O N XVI.

*Distillation of lithrage with acetous acid, with a view to the mensuration of the water formed, as well as to the other products.*

HAVING observed that water thrown on a hot earthen retort of the kind usually sold in London, is absorbed into its whole substance; and that the part of the water which penetrates towards the internal surface, is expelled through it, into the annexed receivers, where it may be condensed; I could not rely on any experiments made in such retorts, in regard to the aqueous products of the charges, since it was to be apprehended that the water, impelled by the excentric pressure of vapour and elastic fluids, might be expelled through the retort much quicker than it is found to enter when poured on the heated vessel: and as the more compact retorts of Mr. Wedgwood might be suspected of imbibing some

water, and perhaps of transmitting it, because they were not glazed; I made the following experiment, with a view chiefly to the water producible in consequence of the union of the empyreal air with the phlogiston of the acid.

I mixed an ounce=480 grains of my strongest concentrated acetous acid with four ounces=1920 grains of water, and this I ground ten ounces 4800 grains of lithrage. Having used the precaution of tying a bladder over the vessel in which the mixture was made, I was assured that there was no waste by the evaporation of the acid, or the emission of any elastic fluid different from the interstitial air of the lithrage, which the water alone would have expelled; and I could not perceive that the mixture was disposed to drink in any of the atmospheric air included in the bladder.

In this confined situation, it became consistent enough in 7 or 8 hours, to be formed into pellets; but to make them pass  
freely

freely and without waste through the long and slender neck of a glass retort, I left them exposed to the air for 24 hours, in which time they dried sufficiently, and lost 168 grains of the water employed. The glass retort, well coated, was filled to the helm with these pellets, and heated on the sand bed of a reverberatory furnace, from which its neck extended two feet, before it entered the receiver, to which it was well fastened with glue lute. The atmospheric air of the vessels is not regarded in the following account, because it passed off with the watery vapour, before any considerable quantity of fixable air was emitted.

cub. in.	fixable	phlogistic
1 ft. 25	13	12 with very little
next 25	19.5	5.5 ditto [inflam.
25	21.5	3.5 ditto
25	22.1	2.9 ditto
25	23.3	1.7
25	23.3	1.7 ditto

At this period the retort was not in the least reddened in any part.



cub. in.	fixable	phlogistic
25	23.7	1.3 ditto
25	24.1	9
25	24.1	9 ditto
25	24.2	8
25	24.2	8 with more in-
25	24.5	5 (flam.
25	24.6	4
25	24.6	4

The mixed airs as they issued smelled like acetous Ether or nit Ether, and water trickled slowly all the time from the neck of the retort, but there was no appearance of oil.

25	24.6	4 ditto
----	------	---------

The retort was not yet reddened.

25	24.6	4 ditto
25	24.6	4 ditto
25	24.8	2
25	24.8	2 ditto
25	24.9	1

The retort was now red hot, and water issued slowly.

25	24.9	1
25	25	0

The

The retort was hotter than would be necessary for the fusion of lithrage, during the emission of the two last measures, which was very slow; and no more could be procured by an encrease of heat until the retort was ready to melt, when I quickly withdrew the fire, and left the vessels to cool gradually. The elastic fluid left in them was fixable air and measured fifty cubic inches, which with the former quantity make 600 cubic inches.

Of this bulk, the fixable air, which was measured as it issued, made 564. 9 cubic inches; but at the mean temperature it would have measured 484. 2 cubic inches, weighing 275. 994 grains.

Of the phlogistic and inflammable air, measured at the mean temperature, after the fixable air was withdrawn from them, there were 35. 1 cubic inches at least, and by the method already described, I found the bulk of phlogistic air to be about 30. 1 cubic inches, weighing 11. 347 grains, and that of the inflammable about 5 cubic

inches weighing at the utmost 1. 305 grains. The distillation was slowly and steadily performed, and lasted four hours in the month of August 1783, from the time when the fixable air appeared until the fire was withdrawn.

The water condensed in the recipient was not in any sensible degree oily, or impregnated with acetous acid, but smelled, not unpleasantly of the inflammable air. It was quite limpid, and including ten grains which adhered to the vessels, it weighed 2107 grains. Of the water mixed with the acid and lithrage, only 1752 grains were included with the charge, because 168 grains had exhaled. In the acid employed the water did not exceed 335 grains, the mere acid being estimated at 145 grains in 480 of this concentrated acetous acid. The whole of the water therefore included with the charge amounted to 2087 grains; which is less than the quantity found in the receiver, by twenty grains. From this alone it appears that a considerable quantity of water was actually formed, and consequently

quently that some of the empyreal air of the lithrage, with phlogiston from the acetic acid, was expended in this way : And the emission of water, during the whole of the process, and long after the charge had sustained a heat sufficient for the fusion of lithrage, cannot be satisfactorily accounted for on any other ground. But it is further to be observed, that a great quantity of watery vapour was waisted out of the receiver, along with the warm elastic fluids ; for whenever I applied a cold and dry vessel to receive them, it was bedewed, and plainly shewed that much more water was really formed in the manner already mentioned, than was ascertained by direct mensuration.

On opening the retort, I found some of the pellets retaining their figure ; but those which lay contiguous to the vessel and were heated more, were altered in this respect. The former exhibited in a distant view, a fallow green colour ; but on closer inspection, this appeared to be compounded of the dark blue of minute globules of lead, interspersed with the yellow of lithrage.

The

The other pellets sunk into a mass consisting of large globules of lead bedded in melted lithrage. A more compleat fusion of the lithrage and subsidence of the lead, in the heat above described, thus appeared to have been prevented by the expenditure of the fire in the formation of the elastic fluids continually emitted from the charge.

The whole mass, carefully separated from the glass, weighed 4560 grains, and therefore the lithrage which was reduced to lead yielded 240 grains of aerial matter; for this lithrage by the mere exposure to the like heat was found to yield little or nothing.

Of the 240 grains, 11. 347 may be considered as the weight of phlogistic air; and 228. 653 grains, is the quantity of empyreal air.

Out of 145 grains of mere acid, 1. 305 were expended in inflammable air; but in consideration of the smell of the water, we may state the expenditure at 2 grains; and then

then it will appear that from 143 grains of mere acid and 228. 6 of empyreal air, 275. 9 of fixable air were formed, and the water composed at the same time was not less than 95. 7 grains, although scarcely a fourth part of this quantity was saved in the recipient.

According to this estimation 82 grains of the empyreal air were expended in forming water, and the remainder of the empyreal air = 146. 6 grains, was employed in the formation of fixable air. But if the materials of fixable air be to each other in the proportion last stated, this quantity of empyreal air was expended in forming 219. 9 grains of fixable air, and the acid furnished the remainder, by virtue of its proper empyreal air.

Now, in comparing the products of different experiments, and allowing duty for inaccuracies, we find strong grounds for suspecting that the proportion of empyreal air to the other matter in fixable air, is variable; and that this, like other acids, may subsist  
with



with different doses of empyreal air, and may vary in this respect, according to the circumstances under which it is formed. This is, at least, a consideration not to be neglected by future experimenters.

## SECTION XVII.

*Regulization of Arsenic by acetous acid.*

THE flame of burning regulus of arsenic, and the facility with which it enters into combustion in a moderate heat, impressed me with the opinion that it contains more phlogiston than is held in lead or metals which exhibit no flame or vivid sparks during the calcination, and that if there is any loss of phlogiston during the calcination of either, that of the arsenic must be greatest. In this case, the calx of arsenic would not only require a greater quantity of phlogisticated acid for its reduction to the reguline state, but would yield a smaller proportion of fixable air; since the fixable air which is formed by the assistance of empyreal air in reductions, is five or six times greater in quantity than that which the acetous acid alone can yield by ignition: But if, on the other hand, the calx of arsenic should

should be found to require but a small quantity of acid, in order to form the combustible regule ; and if the quantity reduced to the reguline state should be proportionate, rather to the quantity of empyreal air expelled from it, than to the quantity of phlogiston derived from the acid, this would show that this regule loses little or none of its phlogiston during the combustion, and receives as little in the reduction.

With these views, and not without expectation of shewing the great quantity of empyreal air which this regule imbibes during the deflagration, without any considerable loss of phlogistic matter, and also of proving the greater affinity of empyreal air to the acid of fixable air, than to that of arsenic, I made the following experiment.

I mixed 1749. 88 grains of my acetated vegetable alkali, whose acid and water weighed 869. 715 and its alkali 880. 165 grains, with 6999. 5 grains of crystalline white arsenic, and gradually heated the

mixture in a glass retort placed in a sand pot and connected with the usual apparatus for measuring the elastic fluids. Rejecting the atmospheric air of the vessels, I stated the product thus.

cub. in.	fix. air	phlogistic
first 9	1.8	7.2
next 9	4	5 phlogistic
9	4.5	4.5 ditto
9	5.5	3.5 ditto
9	6	3 ditto
9	6.5	2.5 ditto
9	6.8	2.2 ditto
9	7.2	1.8 ditto
9	7.6	1.4 ditto
9	8	1 ditto
45	43	2 ditto
45	43.5	1.5 ditto
90	88	2 ditto
90	88.5	1.5 ditto
90	88.5	1.5 ditto
90	88.6	1.4 ditto
90	88.4	1.6 ditto

90	87	3 ditto
90	85.5	4.5 phlogistic
90	84.5	5.5 ditto with very [little inflam.

Water still continued to trickle from the retort, and rolled down in round globules over a thin coat of reddish brown arsenical sublimite, which lined the lower part of the neck of the retort through its whole length, and was afterwards found to be regulus of arsenic chiefly. The elastic fluids carried with them a dense white vapour which soon condensed into white, and partly into reguline arsenic; but still so much arsenic was permanently retained, that the elastic fluid smelled horribly arsenical.

90	84.3	5.7 ditto
90	84.3	5.7
90	84.2	5.8 ditto
90	84.1	5.9 ditto
90	84	6 ditto
90	84	6 ditto
90	84	6 ditto
90	84	6 ditto

90	84	6 ditto
90	84	6 ditto
450	420	30 weakly inflam.
90	84	6 ditto.

The emission of air being very flow, although the heat was encreased until the retort was red hot, very little more was to be expected, and I withdrew the fire to save the retort and its contents.

Of the air left in the retort and recipients 33. 6 were fixable air and 2. 4 cub. inches were phlogistic mixed with a very small quantity of inflammable air. The sum of the cubic inches of warm airs was 2376  
of warm fixable air 2221. 9  
the phlog. and inflam. air at the mean temperature measured 154. 1  
the fix. air contracted in cooling by  $\frac{1}{8}$  of its bulk and measured 1851. 584  
weighing 1055.403 gr.  
The phlogistic air weighed 56 grains  
and the inflammable air about 2 grains.

S The



The water saved in the recipient weighed 460 grains, although the acetous salt, which was dry, could not have yielded more than 430.7 grains. Of the water formed during this process, we may say that about 30 grains were saved: but a much greater quantity was manifestly wasted away along with the fixable air, which issued warm, and deposited moisture, as often as the successive portions of it were tried by cooling them in dry vessels.

In the retort I found 3900 grains of reguline arsenic sublimed and adhering near the helm. The neck of the retort was also lined with the like matter in a powdery form, which with the small portion blown forth into the receiver, weighed 37 grains: and the whole of the reguline arsenic did not exceed 3937 grains.

The mass remaining at the bottom of the retort shewed a granular texture, like that of fine sugar, and had a pearly whiteness. It appeared to have been in a state  
of

of perfect fusion, and tasted like neutral arsenical salt. The retort suffered some superficial erosion at the bottom. I separated this saline arsenical substance into two parts; one consisting of the calx of arsenic unaltered, the other of such arsenical salt as I had often made by digesting white arsenic with caustic vegetable alkaline lixivium; for it became liquid in a boiling heat, plastic and repoy in a weaker heat, and quite hard, like glue, in cooling.

Thus it appeared that the acetous acid was expended in reducing a great part of the arsenic to the reguline state, and in extricating its aerial matter, which the quantity of fixable air shewed to be of the empyreal kind. But as no empyreal air was emitted uncombined; and as the residuary arsenic, whether we consider the portion combined with the alkali, or that which was only detained, remained unaltered, we may conclude that this part contributed little or nothing towards the elastic fluid expelled from the charge, and that 3937 grains of regule of arsenic, in the transition to calx

of arsenic or white arsenic, imbibe about 56 grains of phlogistic air, and as much empyreal air as is necessary for forming 1055. 4 grains of fixable with the quantity of acetous acid here employed. This quantity was estimated at 439 grains of mere acid abstracted from water; but as two grains were expended in inflammable air, only 437 had been employed in forming 1055. 4 grains of fixable air.

In consideration of the fixable air alone, 3937 grains of regulus yielded 618. 4 grains of empyreal air; but in consideration of the water formed, we must allow a much greater quantity of empyreal air to white arsenic, together with the proportion of phlogistic air already mentioned. If the proportion of aerial to reguline matter, were the same in white arsenic and in red lead, the regulus in this experiment could have held or yielded only 486. 5 grains of air.

This loose comparison of the necessary quantities of acetous acid, and of the aerial

al

al matter extricated during the conversion of white arsenic into combustible regulus, and calx of lead into metal, and the expenditure of the phlogiston in forming water, in both instances, are sufficient to shew that the alteration is effected in one as well as in the other by the abstraction of aerial matter; since the expenditure of the phlogistic body is as the quantity of aerial matter extricated, and not as the weight of the reguline or metallic mass produced in these experiments. For these reasons, the gradations we observe in the combustion of metals, regulus of arsenic and phosphorus, depend rather on the quantity of the gravitating matter of empyreal air, which they respectively imbibe, and of the fire consequently extricated, than on any circumstance of dephlogistication. Finally, since acetous acid duly applied is as effectual in the formation of phosphorus and sulphur, with their respective acids, as in that of regulus of arsenic, and in metallic reduction, the attraction of empyreal air to the acid matter of fixable air, is of the strongest kind, and must render the decomposition of fixable air exceedingly difficult.

## SECTION XVIII.

*Products of 16 ounces of lithrage and one of charcoal, during the reduction.*

**S**ELECTED pieces of well burned charcoal of oak were put into a deep earthen vessel called a long pot, and covered to the depth of an inch with powdered charcoal. The pot was well closed with a luted cover, and kept two hours in a heat sufficient to melt silver. Then it was placed in such a manner that the powder might remain red hot for some time after the pieces next the bottom had cooled. This was done, in order to perfect the charring, to make the lower pieces imbibe only the proper inflammable air of charcoal, since they must imbibe something in cooling to prevent their absorbing atmospheric air, and especially to prevent any of the empyreal part of atmospheric air from entering into them,

some

Some of these pieces being briskly reduced to fine powder in a covered mortar, 480 grains of this powder were immediately mixed with 7680 grains of powdered lith-rage, and instantly charged into a coated glass retort, for in other experiments I had observed that such charcoal, more freely and longer exposed to the air in powder, drinks in water from the atmospheric air, and that 480 grains of the powder could imbibe four or five grains from the air in half an hour.

The retort being placed in a reverberatory furnace, with its bottom sunk two inches in the sand, the fire was made to act slowly on it from above downwards. The products during the reduction, exclusive of the dilated air of the vessels, were noted as follows, the fixable air having been measured warm, the rest at the mean temperature.

cub. in.	fix. air	phlogistic.
17	5	12 ditto
17	11	6 ditto

S 4

17



cub. in.	fixable	phlogistic
17	16.5	0.5 ditto
17	16.7	0.3 ditto
17	16.8	0.2 ditto
17	16.8	0.2 ditto
17	16.8	0.2 ditto

Thirty grains of water are now saved in the recipient.

17	16.8	0.2 ditto
The retort is almost red hot.		
17	16.8	0.2 ditto
17	16.8	0.2 ditto
85	84.6	0.4 ditto

The Retort is red hot throughout.

85	84.7	0.3 ditto
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Water drops slowly from the nozzle of retort, and the quantity now collected in the recipient is about 40 grains.

85	84.9	0.1 ditto
85	84.9	0.1 ditto

The

The elastic fluids now issue very rapidly.

cub. in.	fix air	phlogistic
85	84.9	0.1 ditto
85	84.8	0.2 ditto
85	84.8	0.2 ditto

The elastic fluids issue by pulses and the watery vapour is visible at its exit from the nozzle of the retort.

85	84.7	0.3 ditto
85	84.7	0.3 ditto
85	84.6	0.4 ditto

The elastic fluid continues to issue rapidly, and to carry watery vapour, and more water is collected in the recipient, amounting in the whole to seventy grains or more.

85	84	1	{ containing a little inflam.
85	83	2	
85	79	6	{ equal parts of phlog. and inflam.
85	74	11	almost all inflam.
85	68	17	ditto
34	22	12	all inflam.

In

In this last is comprehended the elastic fluid left in the vessels. Although the heat was greatly augmented, the emission was now so slow, that nothing more could be expected by any degree of heat that the retort could sustain; I therefore withdrew the fire. The cubic inches of hot fixable air were 1407.6; of phlogistic and inflammable airs 71.4, of which 44 were inflammable and 27.4 phlogistic air.

By cooling several portions of the fixable air, at different periods of the process, and allowing .57 gr. to each cubic inch of it in the temperate state, I estimated the weight at 650 grains. The 27.4 cubic inches of phlogistic air weighed 10.329 gr. But as it had been excessively agitated with water unusually thickened with lime, I suspected that some of it was entangled in the lime, and had eluded the mensuration. It is therefore expedient to state the phlogistic air at 20 grains, since this will better accord with other experiments, and will create the least error here.

The

The inflammable air measuring 44 cubic inches, was estimated at seven grains, for it was lighter specifically than any that had been expelled from acetous compounds.

The elastic fluids, as they issued, smelled agreeably of fixable air, and of nothing else until the inflammable air appeared, which imparted its peculiar smell to the fixable air that accompanied it. There was not a particle of oil; and eighty grains of water were saved in the recipient, although a considerable quantity was certainly wafted away along with the fixable air; for dry measures were soon bedewed with it in cooling,

When the helm of the retort was broken off, the globular part with its coating appeared like an earthen vessel well glazed on the inside. The glass was not much corroded, but was indented, near the upper part of the charge, by masses of lead: These incircled a much greater quantity of the metal, divided into grains and drops of various

rious fizes, by the interposed charcoal powder.

Having carefully separated the lead and charcoal from the glafs, I found their weight to be 7200 grains, of which the charcoal made more than half the weight of the quantity employed; but how much more I could not ascertain fatisfactorily, becaufe a little of the lead adhered to that which I separated mechanically, and fome of the charcoal followed the lead and was wafte in the fuſion of it. Another circumſtance contributed likewise to prevent my knowing the exact weight of the reſiduary charcoal; for it had imbibed, in cooling, ſome of the fixable air remaining in the receiver, and perhaps a little atmofpheric air.

As the charcoal expended in this operation was certainly much leſs than half an ounce, = 240 grains, and I had found by other experiments ſimilar to that which is next to be related, that 7680 grains of lithrage require only 213. 7 of charcoal for

for the reduction, I have no doubt that this last was the quantity expended.

The quantity of earth and alkali in 213. 7 of charcoal being too small to claim our attention in this place; and the phlogistic air of the lithrage, and the inflammable air of the superfluous charcoal, having contributed nothing to the other products; we may say the empyreal air of the lithrage, weighing 736 grains, together with 213. 7 grains of expended charcoal, produced 650 grains of fixable air, and a quantity of water greatly exceeding that which was saved: and since the weight of the efficient charcoal and of the empyreal air, making 949. 7 grains, exceeds that of the fixable air by 299. 7 grains, this last appears to have been the quantity of water formed, though not all condensed, in this operation.

To form this quantity of water 42. 8 grains of phlogiston are necessary, according to the admirable experiments of Mr. Cavendish; and as there is no reason for  
 sup-



supposing that the charcoal contained more than this quantity, which is  $\frac{1}{3}$  of its weight, of phlogiston, no part of this last appears to have entered the lead, or contributed to the fixable air, or to have been otherwise expended than in the formation of water. By this computation, no more than 171 grains of the expended charcoal, was employed in the formation of the fixable air; and as 256. 8 grains of the empyreal air, were expended in the water, no more than 479. 2 grains contributed to the fixable air; and in 650 grains of it, the empyreal air was to the acid matter as 479. 2 to 170. 8 or as 2. 8 to 1.

This proportion differs considerably from that which was computed, in regard to the fixable air from acetous compounds; but whether the difference is owing to an erroneous estimation of the mere acid in acetous acid, and of the quantity of fixable air which it can yield by heat alone; or to a capacity of the principles of fixable  
air

air to unite in different proportions, when they meet in different circumstances, or with a great excess of one or the other, I cannot yet determine.

S E C-

## S E C T I O N XIX.

*Products in the reduction of lithrage and calx of mercury with the smallest quantity of charcoal.*

**I**N order to avoid the inconveniences arising from an excess of charcoal, and to find the greatest quantity of lithrage that can be reduced by a known weight of it, as well as the produce in fixable air and water, I made the following experiment with 120 grains of charcoal, and 7680 grains of lithrage, prepared and mixed in the manner already described.

A small retort, well coated, and charged to the helm with the mixture, was placed in an earthen vessel, and surrounded with as much sand as filled the space between them, and was sufficient to cover the helm and a part of the neck.

The retort thus secured, was made to stand high above the bed of the furnace, in order that the fire might act equably around the charge, and fuse the lead into one solid mass, of which no part should be lost, although the glass should be penetrated by it. These measures were also intended to produce a steadier emission of the elastic fluids than happened in the preceeding experiment.

Rejecting the atmospheric air of the vessels, I measured the products of the charge gradually heated, thus.

cub. in.	fixable air.	phlogistic air	
first 18	5	13	
next 18	13.2	4.8	{ phlog air with $\frac{1}{10}$ of emp. air.
next 18	15.6	2.4	
			{ phlog. with $\frac{1}{5}$ of emp. air.
18	17.4	0.6	
18	17.8	0.2	ditto
18	17.9	0.1	ditto
18	17.91	0.09	{ phlog. with $\frac{1}{4}$ of emp. air.
	T		After

After the 32 cubic inch of emitted airs, ten grains of water were saved in the recipient, and after this last measure about 25 grains were saved.

54	53.73	0.27 ditto
90	89.55	0.45 ditto
90	89.55	0.45 ditto

Each of these portions in passing in large columns into the common air through water, shewed watery vapour suspended in them, and bedewed the vessels in which they were cooled.

90	89.55	0.45 ditto
90	89.55	0.45 ditto
90	89.55	0.45 ditto
90	89.55	0.45 ditto
90	89.55	0.45 ditto
90	89.55	0.45 { phlog. with $\frac{2}{3}$ empyrean air.
36	35.8	0.2 { equal parts of these.

In this last is included the air left in the vessels whilst they were hot. Towards the end, the emission gradually decreased in velocity, and it ceased at the last cubic inch; although the heat had been more than sufficient for the reduction of litharge, for 15 minutes. The fire was now withdrawn.

The sum of the cubic inches

Of hot fixable air was,	910.74
Of temperate phlogistic air	23.09
Of temperate empyreal air	2.17

The water saved amounted to 49 grains, although a great quantity was certainly carried off by the fixable air, notwithstanding every endeavour to moderate and equalize the heat.

The fixable air, when it had contracted by cooling to the mean temperature, was estimated at 384 grains, at the rate of .57 gr. to a cubic inch; but I strongly suspected that the specific gravity of this fixable air was not so great, and conse-



quently that the absolute weight was less than 384. The phlogistic air weighed 8.704 grains, and as some part of it proceeded from the unreduced litharge, which preyed on the vessel, and yielded some of its empyreal air, the phlogistic air appertaining to the revived litharge may be stated at 8 grains. The empyreal air weighed 0.911 grains.

In the retort I found a cake of litharge, a quarter of an inch thick, vitrified into an opaque yellow slag with part of the glass of the retort, and the erosion extended in some parts through the coating as far as the sand; but yet the toughness of the slag prevented all transpiration in this quarter, for the resistance to the passage of the elastic fluids into the measures, was only an half inch column of water.

Under the litharge I found a mass of lead, and a few large grains which had bedded themselves in the glass, all together weighing 3888 grains. There was not the smallest vestige of charcoal; and as the  
earthy

earthy and alkaline parts of it, were inconsiderable, and were vitrified in the mass already mentioned, they did not retain any aerial matter of charcoal; for by repeated experiments I have found that such vitreous masses, and even the finest flint glass, retain nearly the whole of the empyreal air of litharge, but cannot, in perfect fusion to fluidity, hold any considerable quantity of fixable air.

Not a particle of inflammable air was expelled in this experiment, because the litharge, in the degree of heat necessary for expelling inflammable air from charcoal, furnished empyreal air enough to unite with the inflammable air, and contained a redundancy of air beyond what the inflammable matter of the charcoal required. A little of this superfluous air was expelled by the great heat to which the litharge was exposed and in the act of vitrification, for when litharge forms glass with clay or sand, it parts with a little of its emp. air.

As the lead weighing 3888 grains, yielded 424. 513 of air, of which eight may be accounted phlogistic, the empyreal air of the reduced lithrage, amounted at least to 416. 513. gr. and this quantity with 120 grains of charcoal, making 536. 513 gr. afforded scarcely 384 grains of fixable air, and a quantity of water, which was not less than 152. 513 grains, but might have been more. Towards the formation of this water, from 22 to 24 grains of phlogiston were necessary, which last is a fifth part of the weight of the charcoal, by this approximation we account for as much phlogiston as the charcoal can well be supposed to contain. As the water engaged at least 130 grains of empyreal air, if not more; the fixable air engaged about 287 of empyreal air, and derived about 96 or 97. 5 of acid matter from the charcoal. Thus the empyreal air seemed to be to the acid matter in this fixable air, nearly as 3 to 1; and if the weight of the fixable air had been taken at less than 57 grains in a cubic inch, or its absolute weight had not been overrated by assuming a greater specific gravity than it really possessed

possessed, the proportion of the empyreal air to the other matter of *this* fixable air would be perhaps accurately 3 to 1. Regarding all this only as an approximation to the truth, and trusting that the errors cannot be so great as the difference between 3 and 2, I am of opinion that fixable air formed in these circumstances, contains more empyreal air than is in the ordinary sort, and that whilst some specimens of fixable air have but  $\frac{2}{3}$  of their weight of empyreal air, others have  $\frac{3}{4}$  and differ in specific gravity; the circumstances which afford this latter proportion being, strong heat, and redundancy of empyreal air.

As empyreal air is a common principle of fixable air and of water; and as it actually makes water with the phlogiston of charcoal, at the same moment that the like empyreal air engages other matter of charcoal, and makes fixable air with it, there is no ground for the opinion that phlogiston is a necessary principle of fixable air; but all our experiments conspire to shew, that it consists of the gravitating matter of empy-

real air, combined with that acid principle which is common to acetous acid, oils, coal, vegetables, dense inflammable air, &c.

But as every acid may subsist partially phlogisticated and imperfectly impregnated with empyreal air, so may fixable air; and it is to be expected that future experiments will shew considerable varieties in fixable air, arising from these causes, and discoverable by the specific gravity, the menstrual powers, and the different bulks imbibed by water.

By the quantity of elastic fluids and water, and the total expenditure of the charcoal in the formation of them, it is now pretty certain that litharge loses its aerial matter, but receives nothing in the reduction, and consequently loses none of its phlogiston in calcination: It is therefore highly probable that all calcinations and reductions of metals are effected in the same way.

In the reduction of *mercurius calcinatus* by charcoal, I have found that water is formed as well as in the reduction of litharge, besides the fixable air which Mr. Lavoisier had noticed. But this fixable air did not appear to contain more than  $\frac{2}{3}$  of its weight of empyreal air: and in this instance it is certain that no part of the phlogiston of the charcoal is necessary towards the metalization, because the empyreal air can be expelled, and the mercury may be revived, without charcoal, and by heat alone.

It is impossible for a man who must employ the greater part of his time in the duties of a profession which allows no vacation, to superintend such experiments as those on which the foregoing estimations have been founded, from the commencement to the termination; and being thus circumstanced, I think it necessary to observe, that some part of every one of these experiments and mensurations, was committed to the care and fidelity of my operator. If any unintentional errors on his part should happen to conspire to the encrease of mine,



my estimations may be very incorrect in regard to the proportions ; but I have no reason to doubt that the notions of metallic reduction, of the principles of fixable air and dense inflammable air, and of all that does not depend on accurate proportion, will abide the test of future experience.

## S E C T I O N XX.

*Phenomena of the combustion of dense inflammable air, and of substances containing the acetous and phlogistic principles; and mensuration of the products.*

IN order to fire large charges of inflammable air without waste or danger, I provided glass jars that were strong enough to bear an explosion equal to that of a pistol charge of gunpowder. The cylindrical cavity of each was ten inches in length and one in diameter; and at the distance of  $\frac{2}{10}$  of an inch from the bottom, two holes were drilled at right angles with the axis of the cylinder. Into each of these holes a piece of brass wire,  $\frac{1}{16}$  of an inch in diameter, rounded at one end and ringed at the other, was cemented, so that the distance between the rounded ends within the vessel did not exceed  $\frac{1}{8}$  of an inch, and that  
the

the ring of each wire did not project above  $\frac{3}{16}$  of an inch, for longer pieces were found to be inconvenient.

By these means I could make the electrical spark taken between the wires, to be great or small, according to the size or charge of a Leyden jar, employed for this purpose. That part of each exploding jar, which was to be occupied by an elastic fluid previous to the ignition by the electric spark, was graduated, in order to shew any errors in the mensuration, or waste in the introduction of them ; and also to shew the quantity of elastic fluid remaining after an explosion.

By repeated trials I found that a cubic inch of the due mixture of inflammable and empyreal air, was the greatest quantity that could be fired at once, in an exploding jar of this kind, without waste of the quicksilver in which it stood inverted, and which was impressed and agitated violently at each explosion ; or without manifest loss of the inflamed and dilated airs : And I

was

was convinced that the brass wires had no sensible effect in any of the experiments that I am now to mention.

To hold the exploding jar in the required position, a brass collar was fastened to it by screwing the ends of the collar together, and a piece of brass projecting from the collar, and sliding into a heavy frame of iron, connected the whole, so that the exploding jar might recoil an inch or a little more; but not without moving the whole frame, which resisted with a force of 14 pounds.

After some trials in this instrument, I observed that the inflammable air which was first expelled from an acetous salt by the weaker heat, required almost double its bulk of empyreal air for its combustion, by reason of the ethereal vapour mixed with it, or of its extraordinary density. But that the inflammable air expelled last by the stronger heat, and duly separated from the fixable air, required much less empyreal air, and was of a rarer kind, a cubic  
inch

inch of it weighing scarcely  $\frac{2}{10}$  of a grain: Even this inflammable air suffered a considerable diminution of its bulk by repeated agitation with lime liquor, and by long exposure to water.

The disposition of the inflammable air from acetous salts, to vary thus by time, by the unavoidable washing, and the exposure to water, as well as by the degree of heat in which it is procured, is apt to perplex and mislead the experimenter; for a slight error in regard to the specific gravity of the inflammable air, induces great errors in his estimation of the products after combustion, as may be gathered from the following experiment.

In the exploding jar I fired a mixture consisting of 5. 5 cub. inches of inflammable air of the purest kind from acetous calcareous salt and which had been well washed in lime liquor, and of 7. 5 cub. inches of empyreal air, in separate charges of a cubic inch each, and transferred the residuary air of each explosion into a reservoir,

voir, through mercury. This air measured five cubic inches and was fixable air, which lime liquor readily imbibed, leaving a small bubble of phlogistic air, not worth notice in regard to the weight.

In each explosion the concussion of the apparatus was violent, and the vivid red flame shewed that the charge had at this instant expanded to eight times its former bulk, and depressed the mercury so far, although in the next instant, and quicker than the eye could trace it, the residuary air measured only half the charge: soon after it contracted further by cooling.

The internal surface of the jar, as far as the mercury had been depressed, was moistened; and this with the water which encircled the mercurial column at its surface and contiguous to the jar, shewed clearly that the water formed was a considerable part of the exploded airs. Until it appears that fire gravitates sensibly in the quantity here emitted, we must consider the quantity of water thus formed, to be equal to  
that



that by which the weight of the mixed airs exceed that of the fixable air.

The weight of the empyreal air		
at 42. grains in the cubic		
inch was	-	3. 15 grs
That of the inflammable, at .2 gr.		
in the cubic inch was	-	1. 1
And the weight of both		4. 25
The fixable air, at .57 gr. to the		
cubic inch, weighed	-	2. 85
Consequently the water weighed		1. 4
Mr. Cavendish's ingenious and		
accurate experiments shew that		
one seventh of water is phlo-		
giston, and the remainder		
empyreal air.		
In the formation of 1. 4 gr. of		
water, the quantity of phlo-		
giston expended was	-	.2
And the empyreal air expended		
was	-	1. 2
The part of the empyreal air		
which entered in the com-		
position of the fixable air, thus		
appeared to be	-	1. 95

And

And the quantity of matter  
furnished by the inflammable  
air towards the fixable air  
was about - 0.9 gr.

By other experiments and the same kind of estimation, the empyreal air appeared to constitute more than two thirds of the fixable air, and in some it seemed to be accurately  $\frac{2}{3}$ ; but after all I continued to suspect that the proportions of the principles are not the same in every specimen of the elastic fluid which we consider as fixable air. When the dense inflammable air first expelled from charcoal was used, the result was nearly the same. And from the whole I conclude, that when as much inflammable air of this kind is employed, as can be converted, in the explosion, by the empyreal air, the fixable air consists of one part by weight of the acid matter of acetous acid or charcoal, and nearly or accurately two parts of empyreal air; and almost  $\frac{2}{3}$  of this kind of inflammable air is phlogiston, and the remainder mere acid basis of fixable air, and of acetous acid, charcoal, oils, spirits,

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and of all substances that yield acetous acid or dense inflammable air abundantly.

Nothing appears to warrant the current opinion that fixable air contains phlogiston; but on the contrary the water shews that the attractive forces conspire to the union of the phlogiston with empyreal air, to form water, even in the presence of the principles of fixed air; and the quantity of phlogiston which we trace in the water, being  $\frac{1}{3}$  of the weight of the inflammable air, is as great as can by any experiment hitherto made, be shewn to exist in inflammable air of this specific gravity.

When I used the heavier inflammable air carrying ethereal vapour, it required more empyreal air to burn the whole of it, so that no inflammable residue should appear after the fixable air had been absorbed by lime-liquor; and then the bulk of fixable air was greater in relation to that of the inflammable.

When no more than the necessary quantity of empyreal air was used, the quantity

tity of phlogistic air that appeared after the explosion, did not differ sensibly from that which appeared, by other experiments, to have been introduced in the empyreal air or the inflammable air: It was greatest when I used inflammable air that had issued at the commencement of a distillation, or that had been long exposed to water; or when I used the impure air expelled from nitre; and it was least when the purest airs were used. Therefore the invariable and proper products in the combustion of dense inflammable air with empyreal air, are fixable air, water and fire, and nothing else.

It is well known that charcoal continues to yield dense inflammable air, as long as it is urged with intense heat; and if the experiment were pursued to the utmost extent, the whole of it, except the earth, might be converted into this kind of air. But even from charcoal, the air first expelled by the weaker heat, is heavier than that which is afterwards procured by intense heat. And as the heaviest inflammable air from charcoal or acetous compounds, yields

the greatest quantity of fixable air in combustion; whilst the light inflammable air of metallic solutions yields none, as Mr. Cavendish truly maintains; and as it is certain that phlogiston is a common principle of both, the greater specific gravity of the former is to be imputed to the acid matter.

It seems therefore that the proportions, in which the acid and phlogistic matter are combined, in different specimens of inflammable air expelled from vegetable substances, do vary considerably, and that the denser air, containing the greater quantity of acid matter, is more easily expelled than the rarer, which not only holds phlogiston in greater proportion, but is perhaps more fully saturated with the matter of fire, in consequence of the predominance of phlogiston, and the intenser heat in which it is always formed.

To these causes I would impute the great specific gravity of the inflammable air of oils, spirits, Ether, resinous substances, and

of that which mineral fuel emits at first in distillation; and the singular levity of the inflammable air expelled from coal by intense heat.

In the combustion of divers specimens of inflammable air, with the sole view of satisfying myself that they all could yield fixable air and water, I occasionally used air expelled from nitre by heating it in a coated glass retort. Finding that the first gallon or the second was not so pure as the four subsequent gallons emitted from a pound of the pure salt, and that in the subsequent measures the impurity increased, I reserved the best for use; but even in this the phlogistic air made  $\frac{1}{4}$  of the bulk; for this quantity appeared by Dr. Priestly's test of nitrous air, and by exposing the empyreal air to the solution of calcareous liver of sulphur.

In the use of this air, or of inflammable air equally impure, I found that the phlogistic air introduced in either, suffered little or no diminution in consequence of the ex-



plosion, when the quantity of inflammable air was great enough to employ the whole of the empyreal in the formation of fixable air and water; but when the empyreal air exceeded this proportion, a part of the phlogistic air disappeared: this was found by exposing the products of the explosion, first to lime liquor, in order to separate the fixable air; and then to the solution of calcareous liver of sulphur, which after imbibing the empyreal air, shewed the quantity of the phlogistic.

When I had used the proportions in which of the greatest diminution of the phlogistic air had taken place; the water formed at the same time acquired an acid impregnation, acted on the mercury, and became turbid with it. The most favourable circumstances to the production of this phenomenon were, the redundancy of empyreal air, and the repeated exposure of the whole residue of an explosion, to the shock and flame of subsequent charges.

From these phenomena I concluded two years ago, that the gravitating matter of phlogistic air is contained in nitrous acid, and that phlogistic air in the circumstances now described, contributes to the formation of an acid strongly resembling the nitrous. This did not amount to a clear knowledge of the subject.

But Mr. Cavendish, by a happy train of reasoning from experiments devised by himself, and knowing nothing of those which I have now related, has clearly shewn in the last volume of the Philosophical Transactions, that empyreal and phlogistic air exposed to electric sparks, form nitrous acid; and it is no longer to be doubted that the phlogistic air was thus expended in my experiments, which now serve only to suggest an easy and expeditious method of making nitrous acid from empyreal and phlogistic air, and to shew that flame or due ignition serves as well as the electric spark for this purpose.

But as there was no appearance of nitrous acid whilst the inflammable air predomi-

nated in the charge, we may infer, that empyreal air is attracted more forcibly by the acid matter of dense inflammable air, or of the bodies which yield it, than by that of phlogistic air; and that it is by virtue of this superior affinity, that all vegetable and other substances, abounding in our acid matter, and deflagrated with nitrous salt, engage the empyreal air of the nitrous acid in the formation of fixable air and water, and leave the residuary matter of the nitrous acid in the form of nitrous air or phlogistic air.

Tin imbibes more air in calcination than any other metal; unless we except regulus of manganese or iron, which I have not tried. Sixteen ounces of tin encrease in weight to 20 ounces by calcination: But in calcining filings of tin with empyreal air I could not discover any considerable quantity of fixable air, and iron produced but a little. As we do not find fixable air in the combustions of zinc, or phosphorus of Runkel, or light inflammable air, altho' these are vivid in the highest degree, our  
acid

acid matter is not a necessary agent in combustion, but rather seems to moderate it; for the bodies which yield the greatest quantity of fixable air in combustion; afford the weakest heat and illumination; and this corresponds with the capacity of fixable air to retain a great part of the matter of fire which belonged to its principles, and the inability of water to fix any considerable quantity of the matter of fire belonging to empyreal air and phlogiston severally. Hence it happens that coak makes a much stronger fire than charcoal, altho' the former contains ten times more cineritious matter than the latter; for coak yields lighter inflammable air, and affords less fixable air, and consequently contains less acid relatively to its phlogiston, than charcoal.

In the combustion of charcoal with empyreal air, the expenditure of the latter, in fixable air and water, was always found to be more than thrice the weight of the charcoal. I could now easily ascertain the proportions of these, and even the quantity  
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of the acid and phlogistic matter in this and other bodies ; but as my present purposes are answered by approximation, I think it unnecessary to detain the reader any longer on this subject.

## S E C T I O N XXI.

*Primary notions of the matter of Fire.*

IN order to suggest a more extensive use of the foregoing observations, and to facilitate the explanation of certain phenomena which are yet to be considered, I am now to propose a few necessary notions of the matter of fire.

I. *The kind of matter which impresses us with a sense of heat, and which is capable of expanding and pervading all known bodies, is subject to laws of attraction, which fixes and disguises a certain quantity of it in divers substances; and this matter produces the effects which we call heat, and acts as fire, only when it is extricated from other kinds of matter.*

This notion needs no illustration or support; for the phenomena which conspire  
to



to impress it, are very numerous; and Black, Bergman, Cavendish, Crawford, Priestley, Kirvan, Lavoisier, and other distinguished philosophers, have adopted it.

2. *The homogeneous parts of the matter of fire repel each other.*

This repellent property is apparent in all the processes in which the matter of fire is extricated from the grosser and gravitating parts of bodies. The chief of these processes are the mixtures producing heat, the absorptions of divers cold elastic fluids causing heat, vitriolizations, incalascence of pyrophori, respiration, putrefaction, fermentation, and combustion. In all these, the matter of fire, so soon as it is liberated, is found by its peculiar effects, and the mensurable decrease of heat at increased distances from the source of emission, to move excentrically from that source, and to decrease in density. But as this happens, whether the extrication of it be attended with illumination or not, it indicates nothing that is consistent with  
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the tenour of nature, or that may be suggested by analogy, except that the parts of the matter of fire repel each other, although they certainly are attracted by other kinds of matter. This repellent property is equally apparent in every instance of the formation of elastic fluids from aggregate bodies; and especially when this is done by mere ignition. But as these instances afford another inference of equal use, I shall subjoin them to the following notion.

3. *The matter of fire, by virtue of the repulsion subsisting between its homogeneous parts, and of their attractions to the parts of other matter, is the cause of the elasticity of aeriform fluids.*

This notion is necessary to the solution of the phenomena, and is supported by direct evidence, of which the following part will be sufficient.

Oils, Refins, vegetable acids, charcoal, and divers other bodies, are almost totally convertible into fixable air, and inflammable

ble air by fire. Nitrous acid may be decomposed and converted, in part, into empyreal air, in the remainder into phlogistic or nitrous air, by the agency of fire. The whole substance of solid nitrous ammoniac is convertible into fluids permanently elastic, by the mere action of fire. From the solid aggregation in manganese and other metallic calces and in divers salts, the gross matter of empyreal air may be propelled, to form an elastic fluid, by fire; so may that of dense inflammable air from coak and divers hard bodies; that of fixable air from stony concretes; that of alkaline air from ivory, Prussian blue, and microcosmic salt; that of vitriolic, or of marine, or of hepatic air, from divers solid, saline, or sulphureous compounds. All this is done by fire; and being best effected in vessels that are impervious to every other known matter, amounts to a satisfactory proof that the matter of fire is the only necessary and agent in the conversion of solid bodies into elastic fluids, and in the maintenance of their elasticity.

The electric matter is not to be mentioned in objection, until it is proved that it does not itself consist of the matter of fire, in a certain modification of it, depending on the repulsive property, and the relations to gross matter, which we are now describing.

Seeing this extensive agency of the fiery matter; that we can not only trace it into the subjects which thus become permanently elastic, but that it gives a temporary elasticity to vapours and sublimates; seeing that these resume their aggregation as fast as it escapes from them; that its union in the fluids, to which it gives permanent elasticity, may be further proved by the extrication of it from every one of them; and that, in these liberations of it which are daily experienced, in the absorptions of elastic fluids, in combinations, and in combustions of them, the emission is so copious as to remove all doubt of their having held it in great quantity, united with their respective separated parts, and restrained during that union from acting like liberated fire;

fire; observing also that as fast as the fire is liberated or excluded, the distant grosser parts of elastic fluids rush together or into other bodies; as when empyreal and nitrous air make nitrous acid, or empyreal and light inflammable air make water which cools to solid ice, or marine and alkaline air make sal ammoniac; or as when acid or alkaline airs rush into water, or empyreal air into phosphorus; we cannot now hesitate in admitting that the grosser parts of elastic fluids, as well as those of vapour, are made to recede from each other contrary to their inherent and incessant attractive powers, by virtue of their respective charges of the repellent matter of fire, and consequently by the repulsion of the parts of fire to each other.

4. *The charges of repellent matter, by which attractive and gravitating particles form elastic fluids, are distinct atmospheres of fiery matter, in which the densities are reciprocally as the distances from the central particles, in a duplicate or higher ratio.*

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This is an evident consequence of the former notions, and the prevalence of the repulsive over the attractive forces ; and the terrestrial atmosphere, in which the density is inversely as the squares of the distances from the earth, shews that it is the natural and necessary effect of such forces, to form the charges of fiery matter which the particles engage, into the described atmospheres. The further evidence of the truth of this notion arises from phenomena, which I am presently to consider and explain, and which are not inexplicable by any other condition or agency of the matter of fire, that has been hitherto suggested.

*5. The repulsion of the homogeneous parts of the matter of fire, limits the quantity that can be engaged by bodies, and tends to diffuse the remainder equably in space.*

This notion needs no illustration.

*6. The matter of fire limits the quantities, in which aeriform fluids, and bo-*  
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dies



*dies containing it, can combine chemically.*

In the conversion of solid bodies into elastic fluids, we perceive the repulsive forces of the matter of fire resisting and overpowering the reciprocal attractions of the grosser parts ; and in mixtures of empyreal and inflammable air, and in divers other mixed airs, we see this matter resisting the attractions which tend strongly to the chemical combination of the heterogeneous gravitating particles.

In such instances it is manifest that the sum of the repulsive forces, exceeds that of the attractive.

When aeriform fluids condense each other, or are concentrated and aggregated by bodies, it is equally evident that the attractive forces, although resisted by the repulsive, are prevalent.

These, and divers other phenomena shew, that the natural power, whether attractive  
or

or repulsive, of each part of matter, is limited; and therefore the sum of the powers which any body can exert in regard to another, is by a law of nature as the number of its active parts, or in other words, as its quantity of matter.

In consequence of this law, the sum of the repulsive forces, which resist the approximation of the gravitating parts of an elastic fluid, and their union with those of a body which also holds some of the matter of fire, is as the quantity of that fluid; and no more than a determinate portion of it can be aggregated and combined in the body whose quantity of matter and attractive powers are limited.

By the same law it is determined that elastic fluids shall unite with each other in limited proportions only, to form denser fluids or solid bodies, and that the superfluous quantities shall remain elastic and unaltered.

As the matter of fire is manifestly the agent which resists the coalescence and union of attractive particles in these cases; and as the same matter demonstrably exists in all bodies that unite only in limited proportions, we must ascribe to this only competent and manifest agent, all those limitations which we experience, in regard to the proportions, in which bodies can be chemically united, and which we briefly express by the word *saturation*.

## SECTION XXII.

*Applications of the foregoing notions in the explanation of divers phenomena.*

AS the limits of this Essay do not permit me to make extensive applications of the foregoing notions, I shall endeavour, in the expression of a few, in this and the following section, to suggest every thing that seems necessary towards explaining the most intricate phenomena of the matter of fire.

In regard to the apyrous bodies, such as the pure earthy substances, I would infer from these notions that they chiefly consist of parts which do not attract the matter of fire with forces sufficient to cause a disunion of them, and an interposition of this matter in such quantity as to induce softness or fluidity,

Concerning fusible bodies which concrete in cooling, I would in the next place infer,

that they consist chiefly of parts which attract the matter of fire with forces somewhat greater than those last mentioned, and sufficient to effect the solution of them in the fiery fluid, but not for the permanent retention of it : That bodies of this class exclude the solvent by virtue of the prevalent attractions which tend to reunite their gross parts ; but that they receive and transmit the matter which causes heat, more freely, and they retain it longer, than the former can in similar circumstances, by reason of the stronger attractions.

The bodies which, like oils or water, form elastic vapour, when duly charged with the matter of fire, consist chiefly of parts which attract it with forces still greater, and sufficient to compel atmospheres around the distant molecules ; but yet not sufficient to retain these atmospheres after the influx of fire ceases, and in opposition to the mutual attractions of their central molecules, and the tendency of the fiery matter to diffuse itself equally in the neighbouring spaces. As the  
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thermometer shews no more than the relative quantities of the free matter of fire in bodies, these lately mentioned require a greater quantity of the fiery matter than the former, before they exhibit an equal temperature by the thermometer, for the reason already mentioned.

It is also by virtue of this superior attraction to the fiery matter, that ice, resin, fats, and other vapourable bodies, become fluid by moderate incallescence, but not before they have received a great quantity of fire; and that they respectively evaporate with less ignition or incallescence, in vessels which avert the pressure of the aerial atmosphere, than where that, or any equivalent compression, conspires with their aggregate attractions, to resist the influx of fire and the disjunction of their parts.—Thus water, or spirit, moderately heated, and placed in the receiver of an air-pump, boils when a part of the air which compresses it is drawn out, and ceases as often as the pressure is restored.



Still stronger attractions of the matter of fire, comparatively with the forces which tend to the exclusion of it, are seen in ethereal oils and Ethers : For their vapours cannot be condensed without the aid of compression ; and when they are thus condensed and aggregated, their molecules, by attracting fiery matter and compelling it into atmospheres, with forces superior to those with which they attract each other, are made to recede, and form aeri-form fluids, in the lowest temperatures, so soon as the pressure of the atmosphere is averted.

That the expansion of such ethereal fluids into the aerial form, in the exhausted receiver of an air-pump, is owing to the tendency of their molecules to attract the matter of fire and to form atmospheres of it around them severally, and that it is not effected by any other agency, is apparent from the concomitant phenomenon of *cold* : For as fast as they assume the aerial form, they engage and fix the free fiery matter which belonged to the spaces into which they

they expand; and this privation or deficiency of disengaged fiery matter, is what we call cold.

The bodies which by ignition may be partially or totally converted, even under the atmospheric pressure, into fluids permanently elastic, shew the kinds of matter by which that of fire is attracted in the supreme degree.

For the elasticity which subsists under immense pressure, argues a stronger attraction of the particles to their respective repellent atmospheres, than that which we last noticed; but that this stronger attraction compels denser and deeper atmospheres, may not only be argued a priori, but is experimentally demonstrable by the bulk, which in elastic fluids is the measure of the atmospheres, compared with the gravity, which is the measure of the gross particles; and it is also apparent in the extraordinary quantity of the fiery matter that escapes in the instant of the aggregation of these elastic fluids, or rather of their particles,

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to form consistent bodies ; As when empyreal air is rapidly imbibed by phosphorus, Pyrophorus, Hepar sulphuris, or iron filings and sulphur ; when alkaline air, and divers acid airs, are absorbed by water, or when they condense each other ; or when the rare inflammable air and empyreal air make water, and exclude their matter of fire.

From all this it may be inferred, that in any future table of the affinities of the matter of fire, *pure phlogiston* ought to rank above every other kind of matter ; instead of being omitted, as it is in Bergman's tables, or supposed to have repugnance or apathy to the matter of fire, as Dr. Crawford formerly conjectured. But when this precedence is given to phlogiston, by reason of the extreme levity of the purer inflammable air of metallic solutions, and of the quantity of fiery matter which it emits in the instant of its union with empyreal air, the gravitating matter of this last air must not be placed beneath any other that is now known ; because no air that is free  
from

from phlogiston, is lighter specifically than empyreal air; or emits more fire in the instant of aggregation.

I consider the specific gravity as a safe guide in our investigations of these affinities and of their order, in regard only to the elastic fluids which seem to consist of no more than one kind of gravitating matter engaged in the repellent atmospheres: And of fixable air, dense inflammable air, acid airs, the phlogistic alkaline air, and others, I would observe, that the atmospheres include molecules instead of solitary ultimate parts; for without this chemical union of heterogeneous parts, and the formation of molecules, an elastic fluid of the kind that I now speak of, could not differ, as it does, from either kind of matter of which it is composed.

From this consideration of the attractive forces which tend to form molecules, and of the atmospheres which, in compound elastic fluids, encompass the molecules, but not the ultimate parts severally, we derive

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an easy explanation of the phenomenon so often noticed in the preceding pages; I mean the conversion of a substance, not into one, but into two or three different elastic fluids, by mere ignition.

When elastic fluids are formed in solutions and other processes, in which the subjects are not ignited, it is to be observed that the gravitating parts of the emitted elastic fluid, were distant from each other, by reason of the interposed matter, at the instant of their extrication, and that at this distance there is a great diminution of the powers which restrain them in their tendency to engage all the matter of fire that the menstruum or solvent could extricate during their union. Thus it happens, as Dr. Black originally suggested, and as Bergman has observed in his excellent *Dissertation on Elective Attractions*, that caustic alkali, in the union with an acid, excites great heat, that is to say, in their union they exclude a part of the matter of fire which they severally held in a fixed state; but mild alkali, in uniting with an acid

acid, gives little or no heat, and for this reason; that the gravitating parts of the fixable air, engage all the liberated matter of fire in forming atmospheres around its molecules. This exposition is applicable to every other elastic fluid that is extricated in solutions or combinations attended with little or no incallescence.

Since the particles which attract the matter of fire, exclude a part of their respective charges in the instant of their close approximation or contact, there is no difficulty in accounting for the cold produced in solutions, expansions, and evaporations; in every one of which, the particles which resume the matter of fire, and in fixing it produce the cold, are previously removed to some distance from each other, either by the interposition of the parts of a menstruum, as when ice is dissolved by nitrous acid, or by the prevalent powers of their proper fixed fire, of which we have an instance in Ether placed in the exhausted receiver of an air-pump.



As the mere acetous acid consists of the gravitating parts of empyreal air, of phlogiston, and the acid principle of vegetables; and by the accession of the matter of fire only, makes two different elastic fluids, namely fixable air, and dense inflammable air; it follows from these notions, that the gravitating parts of these two airs would make acetous acid again, with water, if the matter of fire could be withdrawn from them; and I venture to prognosticate that this, or something equivalent, will be done by the first ingenious experimenter that attempts it, either by the means of a body which may absorb the gravitating matter of both, and exclude their atmospheres, or by breaking the atmospheres in the manner which I am to describe in the next section.

There is undoubtedly a natural limitation, as we formerly observed, of the forces with which the gross parts of divers elastic fluids compel, and are compelled by their respective atmospheres; but still these forces are so great, that we cannot form adequate ideas of them, without reflecting

ing on the resistance which they give, even in small quantities of the elastic fluids, to any pressure which tends to condense them, and cause an approximation of their parts; or without adverting to the operations which shew the ability of these forces to maintain the elasticity of divers aeriform fluids, in opposition to the greatest mechanical powers hitherto employed to subdue them. The air-gun, and other instruments exhibit these forces in atmospheric air, and chemical operations and explosive compositions too often shew them in the other elastic fluids.

Although the force of chemical attraction reaches not far from the particles, with any sensible effect, we are not thence to conclude that the attractive virtue ceases at any distance. But from all the known phenomena we may infer, that the attractive forces, tending to the approximation and cohesion of gross particles, decrease in a duplicate, or some higher ratio of the distances, reciprocally; that the natural resistance to the interposition of the fiery mat-

ter, is lessened at the smallest, and totally overpowered at small distances which no eye can measure; and finally, that *where the sensible effect of attraction ceases, there repulsion succeeds.*

## S E C T I O N XXIII.

*Interpretations of the most important phenomena of combustion, according to the foregoing notions.*

AS the atmospheres by which the gross parts of an elastic fluid are made to recede from each other, contrary to their reciprocal attractions, extend into the minute spaces between them, with decreasing density; and as the powers, which form these appropriated charges, compell the several gross parts to the centers of their respective atmospheres, and regulate the position of these parts relatively to each other, as well as their distances; the aerial form is maintained, not by the mere interposition of the matter of fire, but by the intervention of it in the described state of density near the gross particles and extreme rarity at the coincidence or contiguity of the atmospheres.

The nature of the subject admits no inference repugnant to this ; for in a medium of uniform density, the gross particles would be impelled or drawn by equal and contrary powers of the medium, and meeting no resistance in it, to the attractive powers which tend to unite them, they would form an aggregate excluding every part of the medium, except those that might be absolutely coherent with the gross particles and chemically combined.

Therefore, to destroy the elasticity, and to effect the aggregation and union of the gross parts of an aeriform fluid, or of any mixture of different airs, nothing more is necessary than to break or blend the atmospheres into a medium of equal density in the spaces between the particles ; and although this cannot be done by mechanical compression, it is easily effected by replenishing the minute spaces, in which the atmospheres extend, with a denser fiery fluid.

As the smallest spark affords that denser fluid, in quantity sufficient to replenish  
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many of these minute spaces, the fiery matter there expelled, in the instant of the union of the gross parts, extends the necessary ignition through the neighbouring atmospheres, and thus a mixture of empyreal and rare inflammable air; by the momentary agency of a flint-spark; is rapidly expended in the formation of water and the emission of a dense fiery fluid.

As the adventitious fire requisite for exciting the combustion, must have density exceeding that of the atmospheres in their interior densest parts, it is scarcely to be doubted that the greatest density in the atmospheres is almost equal to that of the fiery fluid issuing from a red-hot mass of iron or of earth; for any incombustible body less heated, will not excite combustion in the mixture of inflammable and empyreal air. In this view of the subject, the quantity of fiery matter engaged in the atmospheres, appears adequate to the experienced elasticity of these aeriform fluids, and to all the heat and flame of their combustion.



As the distances of the gross parts of a mixture of empyreal and inflammable air, and the depth and density of their atmospheres, are encreased by heating the mixture gradually, in vessels which do not effectually prevent the expansion of it, the ignition of the vessels to redness, or to any degree hitherto experienced, is found insufficient for the inflammation of the mixture; for the obvious reason of the denser or deeper atmospheres: and on the consideration of all these particulars, I should expect to find a greater degree of ignition, or a larger spark, whether of the electric fluid, or from a burning body, necessary towards the accension of inflammable with empyreal air, when by averting the pressure of the aerial atmosphere, we suffer the mixed airs to expand considerably, than the same mixture would require in the ordinary state of density.

To avoid the tedious enumeration and discussion of phenomena of this kind, I would offer this general rule concerning them: The ignition necessary towards the accension

cension of inflammable air or vapour, in empyreal air, is directly as the density of the repellent atmospheres, and inversely as the attractions of the gravitating parts to each other, for the reasons abovementioned.

In the mixture of inflammable with empyreal air, which do not in the least affect each other, but remain unaltered for any length of time, we see nothing like aggregation to resist the union of their gross attractive parts; and we perceive that the powers which impede their union, are totally different from those by which the gross parts are aggregated into solid bodies. We must therefore refuse our assent to the Chemists who say that the use of ignition in exciting combustion, is to weaken the aggregation of the combustible substance.

That aggregation retards the progress of combustion, is not to be disputed; but to shew why a consistent substance, such as resin or charcoal, may persist in contact with empyreal air, without combustion; and why due ignition causes the inflam-

mation of it, I would say first, in conformity with all the foregoing notions, that phlogistic bodies, whether fluid like oil, or solid like charcoal or resin, contain the matter of fire in a fixed state, and in great quantity; secondly, that although it is thus fixed by prevalent attractive forces, it still repels the like matter of fire appertaining to the empyreal air; because this natural power exists, as well when it is counteracted and subdued, as when it acts unrestrained; thirdly, that the gross parts of empyreal air are prevented from uniting with those of charcoal, oil or resin, by their respective charges or portions of the matter of fire; and lastly, that the effect of ignition is, in regard to the commencement of the combustion, to break and blend the charges of fiery matter which impede the union of the gross particles, as well as to weaken the aggregation of the consistent substances. All this is applicable, in respect to the ignition of nitre with combustible bodies, and the ignition of fulminating powder, fulminating gold, and other fulminating compositions, which require to

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be heated to a certain degree, before they enter into combustion,

When we inflame a combustible elastic fluid or vapour, contained in a vessel, and meeting the open air in a narrow aperture, the progress or velocity of the combustion is as the area of the aperture; because the empyreal part of the atmospheric air is applied in small portions, succeeding each other, but interrupted in the succession by the fixable air or water newly formed. For the same reason the combustion of any aggregate is, in velocity, as the surface presented to air is, in extent; and as the retardation of combustion is not as the hardness of the combustible body, the aggregation is only a secondary impediment.

After adopting these notions of the agency of ignition, and of the causes by which combustion is retarded, we shall find no difficulty in answering the following questions:

Why do light inflammable air and empyreal air, mixed in due proportions, deflagrate totally, and to our sense instantaneously, on the application of a spark or of a body ignited to redness; but not without this ignition? And why are the emission of fire and the formation of water simultaneous?

Why does a mixture of heavy inflammable air and empyreal air, require the like ignition for its ascension, and then deflagrate totally and instantly, and yield fixable air as well as water and fire?

Why does any excessive quantity of empyreal or of inflammable air, beyond the determinate proportions in which their gross parts can combine, remain elastic and unaltered, or not altered in any considerable part of it, after the combustion?

Why do the nitrous alkaline and sulphureous particles of fulminating powder, remain quiescent in the contact of them, until some part of the powder is duly ignited;



nited ; and why does the combustion excited by such ignition, proceed slowly through mixture ? Why do the same materials, when they are more perfectly mixed by fusion, deflagrate with instantaneous and dreadful explosion, in the instant of the contact of a spark with the melted mass ? And why does this mass, when cooled and concremented, deflagrate by the contact of a spark, rapidly indeed, but not so instantaneously as the melted mixture.

Why does fulminating gold, which contains empyreal air, and the phlogistic matter which the volatile alkali introduces, require ignition for its ascension ; and why is the deflagration of it instantaneous ?

Why, in all mixtures of solids, containing phlogiston and empyreal air ; or in gunpowder, which contains empyreal air and phlogiston along with the acid principle of fixable air ; the due ignition of any part is succeeded by the deflagration of the whole ? And why is the combustion the more rapid, as the mixtion and proximity of



of the foregoing active ingredients, are made to approach nearer to perfection, by mechanical comminution and distribution of the subjects containing them.

In replying to these questions, we necessarily furnish answers to thousands that might be proposed, concerning combustions excited by ignition, and regulated by wicks or other means, or accelerated by arts that speed the influx of empyreal air,

In the ignitions that are necessary for the accension of different bodies, we observe many gradations, from that which iron demands, down to the weakest, which is sufficient for exciting combustion in phosphorus of Kunkel, and which, in fair trials of dry and comminuted phosphorus, scarcely exceeds 60 degrees of Farenheit. But in these gradations, we discover nothing but what is referable either to the elective attractions of empyreal air and phlogiston to other gross bodies and to each other; or to the aggregation of the combustible substances; or finally to the incapacity of fire  
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to blend the atmospheres and charges already described, unless it equals or exceeds them in their greatest density.

With regard to the combustions which commence in the coldest air, and without the aid of adventitious fire, we need now say nothing more than that the pyrophori are compounds, which by reason of their extreme sponginess, present surfaces of the greatest extent, to the empyreal air of the atmosphere, and at these surfaces expose to it, in the same instant, the two kinds of matter, namely phlogiston and our acid principle, that attract it with the greatest forces; and that the sum of these forces exerted in such favourable circumstances, is sufficient to overpower the resistance of the atmospheres, and to expel them along with the proper fiery matter of the pyrophori.

In accounting for the spontaneous accension of certain mixtures, such as that of black wad and linseed oil, we are to advert first to the elective attractions of the empyreal

pyreal air, which one of the ingredients always supplies; next, to the phlogistic and acid matter presented by the other ingredient; and lastly to the prevalence of the attractive forces which tend to the formation of water and fixable air and to the exclusion of the matter of fire.

In these cursory interpretations, I have purposely avoided the electrical phenomena; not because they shew any thing repugnant to these notions; nor because they afford no similitudes of the repellent atmospheres, or of the described condition of the matter of fire on the surfaces of bodies, or of the agency of air; nor in consideration of any strong doubt arising in my mind, concerning the identity of the *matter* of fire and the *pure* electrical fluid; but for this reason, that the electrical phenomena are intricate in themselves, and unfit for the explanation of others. The same motives have dissuaded me from the introduction of the phenomena of heat and combustion, producible by friction and percussion.

## S E C T I O N XXIV.

*Of Light.*

**I**N attempting a concise and general exposition of the phenomena which depend on the agency of the matter of fire, I have found it expedient to advert first to those which fall within the chemical department of Natural Philosophy, and to reserve the consideration of Light for this place.

Nothing is more evident than that the fire emitted, during the deflagration of bodies, is a cause of illumination, and that wherever illumination subsists, there is matter in motion. But philosophers do not agree in their opinions of the kind of motion and of the nature of the matter itself.

To exhibit, in a few words, the fallacy of some recent doctrines concerning the  
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matter of fire and light, and at the same time to remove the chief objections which have prevailed with many, as they formerly did in my mind, against the Newtonian Theory of Light, the following observations seem to be sufficient:

In the fiery fluid which is expelled in the manner already described, during the solution or combination of divers bodies; or which is emitted from heated bodies, in consequence of its tendency to equable diffusion; and of the prevalent forces with which the gross parts of such bodies tend to resume their former aggregation; we find every degree of density or heat, from that which corresponds with 540 degrees, at which lead may be melted, down to that of 60 in Farenheit's scale. All this occurs in processes and subjects different from those of combustion; and therefore a great variety, as well as a great number of instances can be produced; to shew that the fiery fluid may flow from bodies, with the smaller or the greater of these densities, without exciting any sensible illumination, or giving light.

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From another train of observations we learn, that light may be produced by the emitted fire, in every state of density, from that which we call temperate, to that of the most brilliant combustions. For light is produced, not only by the vivid deflagration of zinc, iron, or coke, or during the languid combustion of sulphur; but is also sensibly propelled during the slow absorption of empyreal air by cold phosphorus, and the indisputable emission of successive portions of the matter of fire.

The legitimate inference from these phenomena is, not that the matter of light differs from that of fire, but that *Fire* subsists by the proximity, and *Light* by the rapid projectile motion of parts of the same kind of matter: For the latter inference agrees with all the phenomena, whilst the former is repugnant to our experience of the effects of light concentrated by reflection or refraction.

In *Fire*, there is always a motion of the parts, by reason of their tendency to recede



cede from each other, and of their attractions to bodies ; but it may subsist by the density without the motion ; whilst light subsists by the projectile motion, in every density or diffusion of the luminous fluid.

When we consider that the elasticity of aeriform fluids, is owing to the matter of fire ; that a cannon-ball is propelled only by the excess of the repellent powers of parts of this matter, above the forces with which they are attracted by the gross parts of gunpowder, or of the airs emitted during the deflagration of it ; that the velocity of the ball is incomparably less than it would be if it were shot through an unresisting medium ; and that even this latter velocity would be an inadequate representation of that, with which the parts of the fiery matter are shot forth, in the first instant of their liberation from the combustible body which held them closely approximated ; we find the natural powers already described, sufficient in themselves, for the projection of these parts, with all the velocity

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experienced in the light of flaming bodies on earth, and to every distance at which it has been perceived.

In regard to the light of the sun, we need imagine nothing more than the same matter propelled by the same powers, in greater quantity, and with greater vigour, by reason perhaps of a purer and denser atmosphere, and of a greater proportion of the fiery matter relatively to the rest of his substance; for in such circumstances we produce the most rapid and luminous combustions of solid bodies.

In combustions effected by the incumbent air, this acts on the combustible bodies in successive portions, and the matter of light is necessarily projected in like manner, and the parts which succeed each other in the same lines, answer to Newton's definition of a ray of light.

In the rays of light then, we find matter and motion enough to produce all the  
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effects

effects hitherto noticed, on chemical substances, on water, on vegetables, and on solar phosphori.

Having thus traced the matter of fire in various states, to that condition in which it coincides with Newton's character of light, it is unnecessary to insist on the conformity of the foregoing notions with the optical phenomena, further than by remarking that the ethereal medium which affects the surfaces of bodies, and to which he ascribes divers effects, does not appear to consist of any other than the matter of fire, which by the same powers that form atmospheres around the solitary gross parts, must necessarily form a dense elastic medium on the surfaces of their aggregates.

As I have frequently distinguished the parts of other matter from those of fire, by the term *gravitating parts*, it is necessary now to say, that this mode of expression, is not intended to convey an opinion that the matter which attracts so many bodies,  
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does not gravitate to the assemblage of them in our earth, but relates to the *sensible* gravitation of any quantity that we can submit to mechanical trials.

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## SECTION XXV.

*Of fermentation, putrefaction, and respiration.*

THE phenomena of fermentation, putrefaction, and respiration, agree so strictly with these notions, and are so easily explained by them, that it is altogether unnecessary, in the following sketch, to notice any other than the objects of the greatest importance.

Mr. Cavendish has shewn, that from one hundred parts of sugar duly fermented, fifty-seven are expelled in the form of fixable air. Therefore, unless we suppose that the water used in the process is decomposed, which is by no means probable, the conversion of sugar into spirit is effected by the abstraction of 38 parts, or thereabouts, of empyreal air and 19 of acid matter; and the spirit consists of about 43 of phlogistic

gistic and acid matter, combined with some of the water employed in the process: For we need not, at present, regard the small quantity of precipitated earthy matter. The spirit then consists of the vegetable acid principle more fully saturated with phlogiston than it is in sugar, and associated with water; and the superfluous acid matter together with the empyreal air, engaging a part of the matter of fire that is liberated in consequence of these new unions by the mediation of water, escape by reason of the repellent atmospheres.

This perfectly corresponds with the nature of the products of sugar by ignition; for the fixable air which it yields abundantly, shews that empyreal air enters into its composition; the inflammable air, oil, and combustible coal, which it affords, shew all the acid matter and phlogiston that we find in the spirit; and in the earthy part of the charred coal of sugar, we account for that which subsides in the fermented liquor, or may be abstracted in distillation.



The subsidence of earthy matter from a limpid solution of sugar, during the fermentation and new combinations, is easily accounted for in this consideration; that the empyreal air, which is the cause of the menstrual power of acids, is carried off along with that part of the acid principle that is not engaged with phlogiston to form spirit; and that the residuary spirit, or any saccharine acid that may remain, cannot hold the earth in solution.

These general inferences are true, altho' the fixable air might have been over-rated, by its being measured along with the watery vapour which it always carries with it, in these circumstances.

This representation also corresponds with every thing that is worth notice in the preparation and properties of the acid of sugar; for it is prepared in nitrous acid by the abstraction of some of its phlogiston, and by supplying empyreal air to the residuary matter; and the acid of sugar thus constituted, cannot be made  
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to ferment and yield ardent spirit, or any such quantity of oil or inflammable air, as may be had from the sugar.

The changes producible by fermentation, in farinaceous substances, admit of the same concise explanation in regard to the acid and empyreal air extricated, the retention of all the phlogiston with the residuary acid matter in the form of spirit, and the feculent subsidence consisting of earthy, saline, and insoluble fatty matter, or of farina which has eluded the decomposition.

A spirituous liquor, consisting of water and acid matter saturated with phlogiston, contains every principle of acetous acid, except the empyreal air. But this is strongly attracted by the acid and phlogistic matter of the spirit; and therefore by due exposure to atmospheric air or pure empyreal air, or even to that which is held in nitrous acid, the spirituous liquor becomes vinegar, either in the acetous fermentation, or in chemical processes, such as the ingenious and indefatigable *Scheele* has described.

And now the reason is obvious, why vinegar may be made of wine, but no wine of vinegar, by ordinary fermentation; and the answer is easy, in regard to every question that has ever been agitated on the subject of fermentation, unless we except that concerning the agency of yeast and leaven.

Yeast is not always necessary to the vinous fermentation; but when it is used to insure it, under unfavourable circumstances of cold air, imperfect solution of farinaceous matter, or vicidity of the fermentable liquor, it seems to serve only, like the partial ignition formerly described, to give in some part of the mass, a certain preponderance of the forces which tend to the new combinations, over those of the chemical attractions, gravitation, aggregation, and *inertia*, which conspire to maintain the fermentable liquor unaltered. The matter which gives this preponderance, might easily be ascertained by an accurate analysis of yeast. It seems to be acetous acid, already formed, and engaged in magnesian earth and oil, beyond the quantity necessary

necessary for the saturation of the former: for this corresponds with an imperfect analysis of yeast, that I made many years ago; and with the common practice of accelerating the fermentation of ales, by soured ale; and with the use of sour bread or leaven in exciting a speedy fermentation in dough; and with the effect of sour stalks or husks of grapes, or soured casks, in exciting the acetous fermentation speedily, in a vinous liquor; and with the uncommon efficacy which I have experienced of bread soaked in concentrated vinegar, in expediting the conversion of wine to vinegar; the change induced in the vicinity of a small piece of it, being found, in due exposure to the common air, to extend quickly through the whole of the vinous liquor.

The phenomena of putrefactive fermentations vary, with the kinds of matter in the subjects, with the proportions of these, the quantity of water, and the circumstances which contribute to the retention or dissipation of the liberated matter of fire: amongst  
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these circumstances we must rank the partial or free concurrence of the atmospheric air. But neither the incalcsence, nor the fixable air, or the dense inflammable air emitted, nor the dissolution of the organised bodies, nor the waste of their volatile parts, nor the combustions and consumptions which happen in some instances, shew any thing that is not easily deducible from the foregoing notions.

Finally, with the processes, in which fixable air is not only extricated but formed, and in which the matter of fire is at the same time liberated, I must rank that of respiration; in which the thin *reticular* bronchial membrane, rather promotes the agency of the air on the circulating blood, than prevents it by interceding them.

As all the saccharine, farinaceous, herbaceous, and oily vegetable substances, that are used as food, and all the esculent animal substances also, abound with the same acid and phlogistic principles that are contained in our ethereal oil and inflammable



flammable air of acetous acid and ardent spirits ; as these principles form a considerable part of the blood, and are well known to attract empyreal air, even when they are diffused in water and combined with other matter, as it happens in the vinous and acetous fermentations, in putrefactions, and in other processes analagous to these ; the aptitude of the blood to act on empyreal air, might be argued a priori, tho' not so fairly proved as it has been by the experiments first made by Dr. Priestley, and afterwards prosecuted by the Abbe Fontana and Mr. Lavoisier,

An experiment which I made in May 1785, in my public course of Chemistry, and which I afterwards repeated, with the precaution of expiring all the air that I could from my lungs, and of breathing for a while such air as I intended to try, seems to have cleared away all the doubts that attended this subject. It consisted in breathing two gallon measures of empyreal air from nitre, in a glass vessel, poised and moveable in lime-water, so that the air  
within



within was always equally compressed by the atmosphere, under every diminution of bulk by inspiration, and the respiration was made without labour.

The lime water, in which the vessel floated, was further impregnated with perfect lime, and this liquor was constantly dashed and sprinkled through the respired air, by the hand of an assistant, to accelerate the absorption of the fixable air from the residuary elastic fluid; and thus I was enabled to continue the respiration much longer, without interruption, or preparing my lungs anew, than I could otherwise have done. Notwithstanding all this, I could not continue the respiration to the total consumption of the empyreal air, but was obliged to desist at intervals, and to return repeatedly to the respiration, with my lungs prepared as formerly, after the whole of the fixable air had been absorbed by the lime liquor from the remaining empyreal air.

The decrease in the bulk of the respired air, not at all corresponding with the real  
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consumption of empyreal air, and the quantity of phlogisticated air greatly exceeding that which might have eluded my previous trials of the empyreal air, both contributed to shew that some phlogistic air was produced or detached during the process: And now that Mr. Cavendish's experiments prove that the phlogistic air could not have been formed of the empyreal air, I do not hesitate in concluding, that the former was expelled from the lungs during the respiration, along with the matter which contributed to the formation of the fixable air. It therefore is not to be regarded in the present consideration of the expenditure of the empyreal air.

As the pursuit of this last was my chief purpose, and I have not room now for a circumstantial detail of particulars, I shall confine myself to the following report:—After the last respiration, which was maintained with great difficulty and anxiety, the empyreal air disappeared totally, the residue being more phlogistic air, and the fixable air was not equal in weight to the expended

ded empyreal air ; therefore one-third of the empyreal air must have been otherwise engaged.

But from the most general analogy, and from the quantity of watery vapour that issues from the lungs at every expiration, whether we breathe empyreal air or atmospheric air, we may conclude that whilst about two-thirds of the empyreal air were employed in forming fixable air with the acid principle of the oleaginous part of the blood, the remainder of the empyreal air was expended in the formation of water, or perhaps, by some small part of it, in entering the blood : and since a great quantity of the matter of fire is detached, in every process, whether of the mixture of elastic fluids, or putrefaction, or fermentation, or of the solutions of vegetable or animal substances in nitrous acid, or of combustion ; whenever empyreal air is expended in the formation of fixable air or water, and especially when both are composed at the same time ; I see no reason to doubt of the truth of Dr. Crawford's opinion,

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nion, that animal heat is generated in the lungs, and distributed from thence to the rest of the body by the circulating blood : And thus the phenomena of respiration agree perfectly with the foregoing notions of matter.

*F I N I S.*



# C O R R E C T I O N S;

Page. Line.

- 8 2 *for luminated read lami-  
nated*  
21 19 *dele and weight*  
23 15 *for are read were*  
— 16 *for extends read extended*  
29 2 *for more read others*  
30 8 *read the more accurate dis-  
tillations*  
— 14 *after fire add in such quan-  
tity*  
38 15 *dele comma after only*  
39 2 *dele else*  
— 9 *for will read can*  
— 10 *for phlogiston read oil*  
— 11 *dele will*  
— 22 *for acetous read mere*  
45 18 *for heighth read height*  
84 2 *read suppositious*  
— 24 *for fire read the matter of  
fire*  
*The like correction is to be  
made wherever it is ad-  
missible.*  
95 8 *for phlogistic read oleagi-  
nous*  
114 21 *for flacculent read floccu-  
lent*  
133 10 *for nitrous read phlogistic*  
138 3 *for alkohol read oil*  
144 6 *for equaled read greatly*  
146 14 *for visuial read visual*  
154 20 *for contribute read contri-  
butes*  
171 9 *for expells read expels*

Page. Line.

- 172 5 *for protion read portion*  
174 4 *for salts read salt* |  
188 15 *for crystaline read crystal-  
line*  
192 6 *for distills read distils*  
199 8 *and wherever it occurs for  
crystalization read crys-  
tallization*  
202 — *and wherever it occurs for  
lithrage read lithaige*  
204 1 *for vivid read revived*  
— 17 *and elsewhere for Kirvan  
read Kirwan*  
205 6 *for motion read notion*  
208 8 *for calculations read calci-  
nations \**  
— 21 *for imbibe read imbibes*  
210 22 *for tranfaction read transi-  
tion*  
214 8 *for , all read of all*  
219 20 *for detatched read detached*  
225 15 *for aparatus read appara-  
tus*  
229 18 *for think read to think*  
246 10 *for this read with this*  
253 20 *for duty read duly*  
260 22 *for granuilar read granular*  
261 3 *for seperated read separated*  
— 10 *for repoy read ropy*  
291 3 *for finable read fixable*  
296 14 *dele of*  
302 13 *for incalascence read in-  
calescence*







